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Copies of detailed instructions can be had from the Secretary, Imperial Council of Agricultural Research, New Delhi.

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ORIGINAL ARTICLES

THE INFLUENCE OF VARIATIONS IN THE INTERVAL BETWEEN CUTTINGS ON THE YIELD AND CHEMICAL COMPOSITION OF SOME PERENNIAL GRASSES IN THE PUNJAB

BY

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Agricultural Chemist to Government, Punjab, Lyallpur

(Received for publication on 1 December 1941)

THE Chemical Section of the Punjab Agricultural Department has during recent years carried out extensive studies of the nutritive values of natural and cultivated fodders of the province. The results of some of these investigations spread over a period of six to seven years have already been published by Lander [1937] in a bulletin called *Indian Grazing Conditions and the Mineral Content of some Indian Fodders*. A second edition of this bulletin, brought up to date, is in the press.

These investigations have to some extent followed, or been coincident with, work by the Fodder Specialist, in selecting various wild grasses of the province likely to prove valuable under special cultivated conditions.

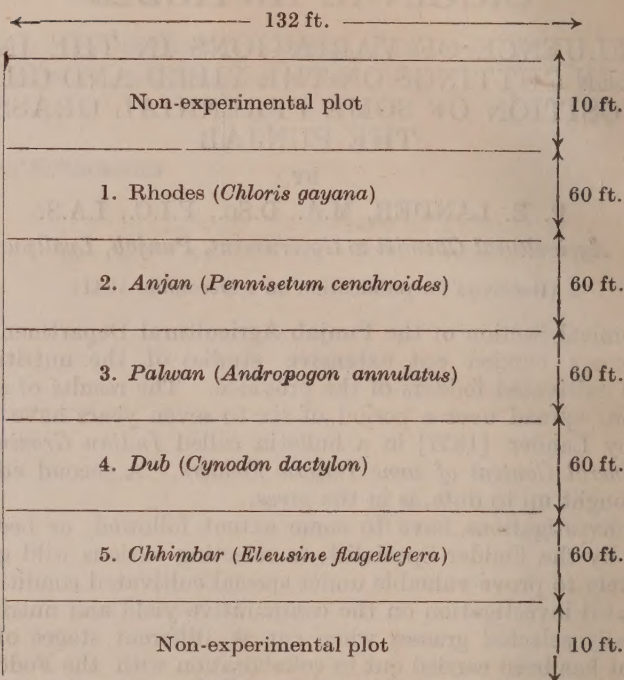
A detailed investigation on the comparative yield and nutritive value of these specially selected grasses when cut at different stages of growth and development has been carried out in collaboration with the Fodder Specialist at the Botanical Sub-station at Sirsa in the Hissar district, a locality which has long been noted for the famous Hissar breed of cattle. In the bulletin referred to above, brief mention has been made of this work and some of the data available at the time of writing given. The investigation has now been completed and the results and conclusions arrived at are presented in this paper.

EXPERIMENTAL

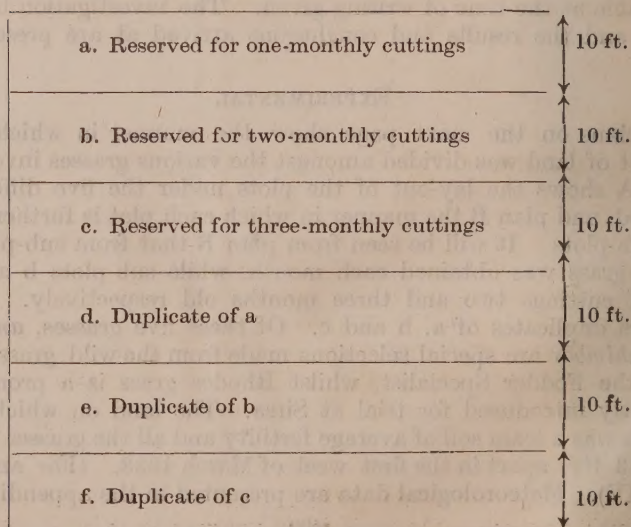
The plans on the next page show the manner in which the experimental plot of land was divided amongst the various grasses investigated.

Plan A shows the lay-out of the plots under the five different grasses investigated, and plan B the manner in which each plot is further sub-divided into six sub-plots. It will be seen from plan B that from sub-plot a, a fresh growth of grass was obtained each month, while sub-plots b and c gave a number of cuttings two and three months old respectively. Sub-plots d, e and f are duplicates of a, b and c. Of these five grasses, *anjan*, *palwan*, *chub* and *chhimbar* are special selections made from the wild grasses of the province by the Fodder Specialist, whilst Rhodes grass is a promising exotic only recently introduced for trial at Sirsa. The land on which the grasses were grown was a loam soil of average fertility and all the grasses were planted in rows 2-3 ft. apart in the first week of March 1938. (For analyses of soil see Table IV). Meteorological data are presented in the appendix.

Plan A



Plan B



SAMPLING AND ANALYSIS

In 1938 the grasses were sampled from June to November and not during the winter months, and as at that time there were no facilities on the spot for estimating moisture, data for total dry matter could not be obtained. Arrangements were made in due course to remedy this defect and in the following year complete data throughout the whole year were collected. Representative samples of grass from each cut were carefully dried at Sirsa for dry matter determinations and sent to Lyallpur for chemical analysis which included protein, ash, acid-soluble ash, lime, phosphoric acid and potash. The data of yield and chemical composition are given in Tables I-III.

DISCUSSION OF RESULTS

YIELD

Table I shows the total yield of freshly cut grasses and the various nutritive constituents obtained per acre during each year. The figures given represent the sum total of the individual yields corresponding to different cuttings obtained throughout the year in accordance with the rotations already mentioned.

GREEN HERBAGE

It will be seen that *palwan* gave the highest yield of green grass and was followed by Rhodes and *anjan* whose yields were almost equal. *Dub* and *chhimbar* gave only about one-third the yield of *palwan* and do not compare with it or with Rhodes and *anjan*. If we consider the effect of the length of the interval between any two cuttings on the yield of grass, it will be seen that, except in the case of *dub*, the yield of green grass is greater the longer the interval between cuttings. This was especially noticeable in the case of *palwan*, Rhodes and *chhimbar*. These results are in agreement with those obtained by Paterson [1933 ; 1935] for some tropical grasses and Woodman *et al.* [1929] for pasture grasses in temperate regions.

DRY MATTER

In computing the nutritive requirements of animals the usual procedure is to base estimates on the dry matter of the feed given and not on the total bulk of the green material. This is an important point to be borne in mind in view of the fact that the total yields of dry matter obtained are usually greater the longer the interval of time between any two cuttings. If we consider a single entire experimental period it will be seen from Tables I and II that there was a greater total quantity of grass obtained after longer intervals and also that the percentage of total dry matter was greater. As a general rule it may be said that in the case of these grasses the yield of dry matter is proportional to the yield of green grass.

PROTEIN

The data for the two years given in this paper indicate a tendency for varieties which give the highest yields of dry matter to give also the highest

TABLE I
Yield of grass and its various constituents at different stages of maturity

Serial No.	Description	Yield in maunds per acre					Percentage variation from the monthly cutting				
		1939-40									
		Grass	Dry matter	Protein	CaO	P ₂ O ₅	K ₂ O	Grass	Dry matter	Protein	K ₂ O
1	Rhodes, one-monthly	143.7	45.28	3.263	0.400	0.332	0.818				
2	Rhodes, two-monthly	145.8	49.32	2.652	0.433	0.327	0.709	+1.46	+8.9	-24.0	-13.3
3	Rhodes, three-monthly	157.4	77.69	2.993	0.621	0.430	1.035	+9.53	+71.6	-17.4	+26.5
4	Anjan, one-monthly	134.4	41.44	3.311	0.339	0.336	1.407				
5	Anjan, two-monthly	147.1	45.35	2.581	0.331	0.340	1.346	+9.45	+9.4	-22.1	-4.3
6	Anjan, three-monthly	152.7	63.65	2.657	0.542	0.429	1.530	+13.62	+53.5	-19.8	+8.7
7	Pakuan, one-monthly	167.5	62.12	4.798	0.393	0.231	1.250				
8	Pakuan, two-monthly	192.3	77.57	3.923	0.441	0.230	1.316	+14.8	+24.9	-13.2	+5.3
9	Pakuan, three-monthly	190.3	102.79	4.057	0.571	0.313	1.600	+13.6	+65.5	-13.4	+28.0
10	Dub, one-monthly	63.1	33.09	2.133	0.245	0.165	0.436				
11	Dub, two-monthly	59.6	30.30	1.385	0.235	0.138	0.364	-5.6	-8.4	-30.4	-25.1
12	Dub, three-monthly	61.0	33.44	1.697	0.317	0.171	0.438	-3.3	+16.2	-20.4	-9.9
13	Chimbar, one-monthly	28.5	16.27	1.411	0.131	0.100	0.252				
14	Chimbar, two-monthly	35.2	17.52	0.894	0.149	0.099	0.203	+23.5	+7.7	-36.6	-17.5

TABLE II
Average composition of grass at different stages of maturity

Serial No.	Description	Dry matter (per cent)	Percentage oven-dried material				P ₂ O ₅ /CaO equivalent CaO : 1	Percentage variation from the monthly cutting			
			Protein	CaO	P ₂ O ₅	K ₂ O		Protein	CaO	P ₂ O ₅	K ₂ O
1939-40											
1	Rhodes, one-monthly	31.5	8.00	0.88	0.73	1.81	0.93				
2	Rhodes, two-monthly	33.8	5.38	0.90	0.66	1.44	0.87	-32.8	+2.3	-9.6	-20.5
3	Rhodes, three-monthly	49.4	3.85	0.80	0.55	1.33	0.81	-51.9	-9.1	-24.7	-26.6
4	Anjan, one-monthly	30.9	7.99	0.82	0.81	3.39	1.17				
5	Anjan, two-monthly	30.8	5.69	0.84	0.75	2.97	1.06	-23.8	+2.4	-7.4	-12.4
6	Anjan, three-monthly	41.7	4.17	0.85	0.67	2.40	0.93	-47.8	+3.7	-17.3	-29.2
7	Paluan, one-monthly	37.1	7.72	0.64	0.45	2.01	0.83				
8	Paluan, two-monthly	40.3	5.06	0.57	0.30	1.70	0.62	-34.5	-10.9	-33.3	-15.4
9	Paluan, three-monthly	54.0	3.95	0.56	0.30	1.56	0.63	-43.8	-12.5	-33.3	-22.4
10	Dub, one-monthly	52.4	6.45	0.74	0.50	1.47	0.80				
11	Dub, two-monthly	50.8	4.57	0.78	0.46	1.20	0.70	-29.1	+5.4	-3.0	-13.4
12	Dub, three-monthly	63.0	4.41	0.82	0.45	1.14	0.65	-31.6	+10.8	-10.0	-22.5
13	Chimbar, one-monthly	57.1	8.67	0.81	0.62	1.55	0.90				
14	Chimbar, two-monthly	49.8	5.10	0.85	0.57	1.19	0.79	-41.2	+4.9	-3.1	-23.2
15	Chimbar, three-monthly	69.5	4.75	0.90	0.52	1.21	0.68	-45.9			

TABLE III
Yield and average composition of grasses at different stages in different seasons of the year

Serial No.	Description	Dry matter (per cent)	Per cent oven-dried material				Yield grass, md. per acre
			Protein	CaO	P ₂ O ₅	K ₂ O	
Summer (April-September)							
1	Rhodes, one-monthly	32.1	7.66	0.86	0.71	1.85	111
2	Rhodes, two-monthly	33.2	5.15	0.84	0.62	1.48	111
3	Rhodes, three-monthly	53.6	3.67	0.77	0.52	1.30	119
4	Anjan, one-monthly	31.6	7.65	0.81	0.76	3.40	97
5	Anjan, two-monthly	31.3	5.30	0.82	0.71	3.05	111
6	Anjan, three-monthly	45.2	3.79	0.83	0.66	2.50	112
7	Palwan, one-monthly	38.0	7.60	0.64	0.44	2.04	121
8	Palwan, two-monthly	41.0	5.02	0.57	0.28	1.68	142
9	Palwan, three-monthly	57.4	3.96	0.54	0.30	1.58	145
10	Dub, one-monthly	53.9	6.48	0.73	0.48	1.48	49
11	Dub, two-monthly	51.7	4.41	0.76	0.45	1.21	52
12	Dub, three-monthly	64.4	4.27	0.81	0.44	1.14	55
13	Chhimbar, one-monthly	59.7	8.69	0.78	0.60	1.57	24
14	Chhimbar, two-monthly	50.1	4.96	0.84	0.56	1.19	31
15	Chhimbar, three-monthly	72.0	4.65	0.89	0.51	1.21	34
Winter (October-March)							
1	Rhodes, one-monthly	29.5	9.28	0.97	0.84	1.64	32
2	Rhodes, two-monthly	36.0	6.04	1.06	0.78	1.32	35
3	Rhodes, three-monthly	36.0	4.70	0.94	0.73	1.50	37
4	Anjan, one-monthly	28.8	8.96	0.85	0.95	3.37	37
5	Anjan, two-monthly	29.4	7.03	0.91	0.87	2.70	35
6	Anjan, three-monthly	31.6	5.70	0.95	0.74	2.02	40
7	Palwan, one-monthly	34.8	8.07	0.66	0.50	1.95	46
8	Palwan, two-monthly	38.6	5.16	0.55	0.35	1.75	50
9	Palwan, three-monthly	43.0	3.90	0.65	0.33	1.46	45
10	Dub, one-monthly	46.9	6.32	0.79	0.57	1.42	18
11	Dub, two-monthly	44.5	5.99	0.91	0.49	1.14	6
12	Dub, three-monthly	50.5	6.08	1.04	0.47	1.07	5
13	Chhimbar, one-monthly	41.2	8.52	1.01	0.71	1.36	4
14	Chhimbar, two-monthly	47.0	6.38	0.98	0.63	1.21	3
15	Chhimbar, three-monthly	52.5	5.63	0.97	0.63	1.19	5

TABLE III—*contd*

Serial No.	Description	Dry matter (per cent)	Per cent oven-dried material				Yield of grass in md. per acre
			Protein	CaO	P ₂ O ₅	K ₂ O	
Summer (April-September)							
1	Rhodes, one-monthly . . .	27.5	7.50	0.74	0.76	1.78	78.2
2	Rhodes, two-monthly . . .	38.8	4.89	0.66	0.63	1.50	93.7
3	Rhodes, three-monthly . . .	41.6	3.66	0.60	0.59	1.13	110.2
4	Anjan, one-monthly . . .	24.9	7.58	0.74	0.84	3.70	106.1
5	Anjan, two-monthly . . .	30.7	5.45	0.70	0.61	3.05	119.4
6	Anjan, three-monthly . . .	40.6	4.09	0.79	0.62	2.10	115.3
7	Palwan, one-monthly . . .	34.6	6.24	0.66	0.47	1.95	101.1
8	Palwan, two-monthly . . .	38.8	4.02	0.61	0.34	1.60	125.8
9	Palwan, three-monthly . . .	47.0	2.58	0.55	0.25	1.04	162.8
10	Dub, one-monthly . . .	49.4	5.93	0.80	0.56	1.50	17.4
11	Dub, two-monthly . . .	52.8	4.95	0.78	0.49	1.24	18.8
12	Dub, three-monthly . . .	52.2	4.95	0.83	0.48	1.15	17.8
13	Chhimbar, one-monthly . . .	42.4	7.22	0.81	0.71	1.38	11.3
14	Chhimbar, two-monthly . . .	47.8	5.73	0.86	0.67	1.23	13.1
15	Chhimbar, three-monthly . . .	53.4	5.03	0.84	0.67	1.13	14.8
Winter (October-March)							
1	Rhodes, one-monthly . . .	30.3	9.74	0.91	0.98	1.62	19.2
2	Rhodes, two-monthly . . .	33.3	6.81	0.89	0.89	1.48	34.4
3	Rhodes, three-monthly . . .	35.1	4.86	0.98	0.81	1.39	38.7
4	Anjan, one-monthly . . .	28.9	8.42	1.03	1.06	3.11	26.9
5	Anjan, two-monthly . . .	30.7	6.79	1.12	1.00	2.67	36.5
6	Anjan, three-monthly . . .	33.0	5.11	1.20	0.86	2.30	38.8
7	Palwan, one-monthly . . .	35.8	6.21	0.80	0.51	1.53	28.0
8	Palwan, two-monthly . . .	38.8	4.87	0.73	0.40	1.35	31.0
9	Palwan, three-monthly . . .	40.4	3.52	0.77	0.35	1.30	45.6
10	Dub, one-monthly . . .	50.7	6.35	0.94	0.56	1.20	4.6
11	Dub, two-monthly . . .	53.9	5.73	1.08	0.52	1.03	4.3
12	Dub, three-monthly . . .	57.3	5.81	1.08	0.50	1.16	4.5
13	Chhimbar, one-monthly . . .	44.5	8.20	1.12	0.90	1.24	2.0
14	Chhimbar, two-monthly . . .	44.6	6.90	1.21	0.78	1.03	2.6
15	Chhimbar, three-monthly . . .	48.4	6.34	1.13	0.80	1.13	3.1

yields of protein, but the data for the two successive years are not consistent. In 1939-40, although the total monthly cuttings of all the grasses under trial yielded less dry matter than the two and the three-monthly cuttings, the higher protein content of the young grass (Table II) more than counterbalanced the effect of the lower yield, with the result that the monthly cuttings gave a greater protein yield in that year. It was further found that three-monthly cuttings gave a greater sum total of protein than the two-monthly cuttings. This finding, however, did not hold strictly true in 1940-41 when the yield of protein in the monthly cuttings was not consistently greater in all cases. This may be explained by the fact that in the case of some varieties the percentage increase of green grass and dry matter in the case of two and three-monthly cuttings was much greater in 1940-41 than in 1939-40, and consequently the higher protein content of the individual monthly cuttings did not match the high protein resulting from the greater yield of dry matter in 1940-41.

LIME, PHOSPHORIC ACID AND POTASH

It will be seen that as the interval between any two cuttings increases the sum total yield of lime is greater, but the variations in the total yields of phosphoric acid and potash were not regular. The data obtained therefore do not yield any conclusive evidence that different cutting rotations have any pronounced effect on the total yield of either of these two constituents.

CHEMICAL COMPOSITION

The results of the mean chemical composition of the various grasses cut at different intervals of time are given in Table II, in the construction of which the original data and the absolute amounts of the various constituents obtained from different plots for an entire year have been employed. The figures for mean composition given in Table II have been arrived at by dividing the total amounts of the various constituents by the total amounts of dry matter and expressing the former as percentages of the latter. It will be seen that there are definite variations in the percentages of some of the chemical constituents in the grasses, e.g. *anjan* is particularly rich in potash, while *paluan* is very poor in both lime and phosphoric acid. With these exceptions, however, there appear to be no major differences in the chemical composition of any of these grasses from similar cuttings. In regard to differences in chemical composition when grasses are cut after varying intervals of time, it will be seen that :—

1. There was a progressive increase in the percentage of dry matter as the interval between any two cuttings increased.

2. The percentage of protein, phosphoric acid and potash decreased with increasing intervals of time between cuttings, the decrease being more marked in the case of protein.

3. The percentage content of lime appears to be independent of time intervals but there is sometimes a slight fall in the lime content and at others a slight rise.

RATIO OF LIME AND PHOSPHORIC ACID

While the functions of both lime and phosphoric acid in fodders has been recognized for long, the far greater importance of the ratio of the two

only been brought into prominence in recent years. Crowther [1939] suggests that this ratio should be 1:1.5 expressed as equivalents of CaO P_2O_5 , because this is the ratio in which these two minerals exist in milk. It has accordingly been calculated and given in Table II as phosphorus-equivalents. It will be seen from these figures that although none responds with the standard figures mentioned above, the monthly cuttings in *Junjan* and *Rhodes* in the 1940-41 season approached nearest to the standard. It will be further noted that as the intervals between the cuttings increased, the ratios tended to deviate more from the standard, because, as already pointed out, as the interval between cuttings increases the phosphoric acid content decreases but the lime remains more or less constant, thus introducing a deviation in the ratio of these constituents. This is a very important point because although, as we have seen earlier, longer interval between cuttings increases the total yield of dry matter it nevertheless disturbs the very important lime-phosphorus ratio.

EFFECTS OF SEASON

The effect of variations in the season on chemical composition is clearly brought out in Table III. The data from two arbitrary periods, viz. summer, from April to September, and winter, from October to March, have been compared and the mean composition of the grasses for the two periods calculated on the same lines as were adopted in the construction of Table II.

It will be seen that the total yield of fresh grasses obtained in the winter period is much less than that obtained during the summer period, the ratio being from one-third to one-fourth. This would naturally be expected as growth is much more luxuriant during the high temperature and monsoon rains of summer than in winter. Woodman and Oosthuizen [1934] have reported on the chemical composition of winter and summer pasture grasses in England, where the winters and summers are not comparable with Indian winters and summers. It would be more strictly accurate to compare the English summer with the Punjab winter from a climatic point of view. These observers found in the case of English pasture grasses that the summer crop is richer in protein, phosphoric acid and lime than the corresponding winter crop. Data for the Punjab show that although the yield of grass is less during winter, it is nevertheless richer in the above-mentioned constituents. During summer the high metabolic activity of the plant material is directed more to the formation of carbohydrates than protein material and the absorption of calcium and phosphorus by the roots. This naturally results in a picture of the chemical composition of the winter and summer grasses, the reverse of that found in temperate climates. An interesting point which is worth attention is the fact that although the Punjab winter grasses of from one to two months old were richer in nitrogen, calcium and phosphorus than summer grass, they were poorer in their potash content. In the case of grass which was three months old, however, the content of potash in the winter grass was greater than that in the summer grass of similar age. Some explanation may be found for the high potash content of summer grasses in the necessity of the plant to meet particular seasonal requirements. During summer photosynthetic activity is greater than in winter and as potash is

TABLE IV
Soil analyses
(Plots 1-5, Plan A)

Serial No.	Description	10 per cent water extract						Mechanical analyses					
		Total solids	Na ₂ CO ₃	NaHCO ₃	NaCl	Na ₂ SO ₄	Ca	Clay 0.00-0.002 mm.	Silt 0.002-0.02 mm.	Fine sand 0.02-0.2 mm.	Sand 0.2-2.0 mm.	Gravel above 2 mm.	Calcium carbonate
1	1st plot, 1st ft.	0.120	Nil	0.076	0.027	0.017	0.016	15.24	13.44	70.09	Nil	0.56	1.23
2	" " 2nd "	0.132	"	0.076	0.028	0.010	0.017	18.39	17.10	63.62	"	0.50	0.90
3	2nd " 1st "	0.110	"	0.076	0.025	0.007	0.016	15.20	16.52	66.63	"	0.17	1.65
4	" " 2nd "	0.140	"	0.076	0.039	0.007	0.021	22.52	21.44	54.14	"	1.04	1.90
5	3rd " 1st "	0.124	"	0.076	0.032	0.009	0.018	16.16	13.36	68.43	"	3.69	2.05
6	" " 2nd "	0.128	"	0.076	0.035	0.006	0.034	19.92	20.34	55.26	"	4.34	4.48
7	4th " 1st "	0.159	Traces	0.076	0.062	0.011	0.019	16.18	10.18	71.91	"	0.37	1.73
8	" " 2nd "	0.176	Nil	0.076	0.076	0.013	0.024	20.02	18.34	55.41	"	0.92	6.33
9	5th " Bore A, 1st ft.	0.148	"	0.076	0.056	0.018	0.018	15.24	10.80	72.58	"	Nil	1.38
10	" " "	0.164	"	0.076	0.069	0.010	0.018	18.28	14.48	62.79	"	4.96	4.45

considered to play an important part in regulating this particular activity, the content of potash in summer would naturally be expected to be greater compared with other food constituents.

SUMMARY

The paper describes the effects of intervals of cutting and of season on the yield and chemical composition of some important perennial grasses in Punjab.

Longer intervals between two cuttings gave greater yields of both green herbage and dry matter.

A progressive fall of protein, phosphoric acid and potash contents of dry matter in the grass occurs with increasing intervals of time between cuttings.

Varying intervals of time between cuttings do not affect the lime content of grasses.

Grasses yield much more dry matter in summer than in winter, but green herbage obtained in summer was poorer in protein, calcium and phosphorus than the corresponding herbage obtained in winter.

Although young herbage obtained in summer was poorer in its calcium and phosphoric acid contents, it was richer in potash than the winter herbage.

From the point of view of the yield of dry matter, the grasses investigated may be arranged in the order: *palwan*, *anjan* (and *Rhodes*), *dub* and *ambar*; with respect to the calcium and phosphorous contents, however, *ambar* comes last, the rest not showing any significant differences.

ACKNOWLEDGEMENTS

The writer is indebted to Mr H. R. Saini, then Fodder Specialist at Sirsa, for growing and collecting the grasses, to Dr Ramji Narain, Assistant to the Agricultural Chemist, for valuable help in calculating and interpreting data. S. Atam Singh, Agricultural Assistant, for analytical work.

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APPENDIX
Meteorological data for Sirsa

Month	1939			1940			1941			Normal (average) rainfall (in.)
	Rainfall (in.)	Mean maximum temperature (°F.)	Mean minimum temperature (°F.)	Rainfall (in.)	Mean maximum temperature (°F.)	Mean minimum temperature (°F.)	Rainfall (in.)	Mean maximum temperature (°F.)	Mean minimum temperature (°F.)	
January				1.29	68.59	36.90	2.40	69.06	43.79	0.60
February				0.29	72.0	39.71	0.15	81.91	51.91	0.36
March	1.02	74.95	44.62	0.19	83.2	51.22	...	90.5	62.93	0.42
April	92.16	58.93	0.09	99.9	64.69				0.28
May	107.03	77.80	0.02	112.6	77.41				0.53
June	2.59	100.94	76.50	3.15	109.9	85.11				1.66
July	0.54	98.24	84.88	1.94	104.84	86.94				3.57
August	102.53	78.69	3.94	98.54	83.26				3.07
September	101.9	74.13	0.35	93.85	83.83				2.41
October	95.74	61.74	...	89.25	73.60				6.25
November	83.68	44.53	...	91.17	53.28				0.05
December	75.44	35.19	...	77.66	46.51				0.34

SOME OBSERVATIONS ON THE GROWTH OF THE
COCONUT FRUIT WITH SPECIAL REFERENCE
TO SOME OF THE CHANGES UNDERGONE
BY THE FIBROUS CONSTITUENT
OF ITS MESOCARP

BY

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(Received for publication on 2 August 1941)

(With two text-figures)

IN view of the facts that the coconut, unlike many other fruits, is composed of several physically and chemically distinct components, that each of these components has unique economic value, and that the fruit takes normally more than a year to ripen and fall down, it was thought expedient to trace the growth of the fruit with particular reference to the changes occurring in its several components. It is true that fairly detailed descriptions of the growth of the fruit are found in such classical treatises on the coconut palm as those of Peland [1931], Sampson [1923] and others, but those studies have not been of the strictly scientific type involving due insistence on all possible measurements and analyses. The present study is an attempt to exclude that serious defect and indicate a possible line of successful attack of several problems relating to the growth of this important agricultural product.

MATERIAL AND METHODS

It is a matter of familiar observation that coconuts belonging to the same bunch make the greatest approach to uniformity. Nuts of the same bunch are very nearly of the same age. Further, equidistribution of nourishment is assured among these nuts, and they undergo identical vicissitudes of atmospheric and soil conditions. The approximate uniformity of the nuts in regard to shape, size and weight is to be attributed to these causes.

There is a general rule that the spacing in time of any two consecutive bunches on the palm is almost a constant, viz. a month. Whatever may be the value of this rule in general practice, it is undependable for rigorous scientific study. Conclusions drawn, therefore, from the measurements and analyses of nuts picked from different bunches of the tree at the same time are lacking in exactitude. Moreover, it has been observed that the coconut fruit is extremely sensitive to weather conditions, and inasmuch as different bunches have experienced different states of the weather, new factors creep in and vitiate the records set up by the mere passage of time.

In view of these factors, the method was adopted of keeping under observation the same bunch for a period of about 12 months during which period the nuts constituting the bunch grew from infancy and reached maximum

maturity on tree. The bunch with the largest formation of nuts was selected and on a specific date of each successive month a man was sent up the tree and a nut detached from the bunch. This nut was then measured and analysed in accordance with the scheme embodied in the tables. For the purpose of confirmation of results and of conclusions drawn therefrom, the experiment was conducted on three trees, and two bunches were marked on each tree.

The nut was weighed immediately after picking, and its volume determined in a specially constructed over-flow jar, a lead sinker of known volume being used whenever necessary. The kernel was scooped or cut out of the shell required and weighed in the raw state. The husk was torn to pieces and boiled in about 2-3 litres of water with 5-10 gm. of sodium sulphite, for a couple of hours, when it softened to such an extent as to render possible the separation of the fibrous from the non-fibrous matter by simple mechanical means. After separation and thorough washing, each component was dried and weighed.

Before determining the specific gravity of the fibre and subjecting it to chemical analyses, a further purification was effected by boiling the fibre in divided fibre with 20 per cent acetic acid for half an hour, followed by repeated washings with distilled water, this procedure having been found suitable from previous work of the author [Menon, 1935]. The fibre was then dried, and after air-conditioning stored in a stoppered bottle.

Determination of the specific gravity of the various samples of fibre presented difficulty at first. Using the well-known method of the specific gravity bottle, it was found that there was no early limit to the time for which bubbles of air escaped from the immersed fibre. Consequently, values obtained by this method on the same sample disagreed profoundly. Complete satisfaction was secured, however, when the fibre was first boiled in a beaker with distilled water for about 15 minutes, when all the capillary air was expelled and the particles settled down. The beaker with contents was then rapidly cooled and the fibre transferred into the specific gravity bottle by means of balance forceps. The bottle was then filled with water, stopper replaced, and weighings made as usual. The fibre was carefully shaken out from the bottle into a filter cone, which was later dried in the oven. The dry fibre was next transferred into a weighing tube, which was then introduced into a special drying apparatus by the aid of which its bone-dry weight was determined. This value represented the weight of fibre in the specific gravity calculation.

Lignin and furfural values recorded in Tables IV and V are based on bone-dry fibre, and were estimated by the familiar 72 per cent sulphuric acid and Tollen's methods respectively.

DISCUSSION

Figs. 1 and 2 throw light on the value of the method adopted for tracing the growth of the coconut fruit.

When measured in C. G. S. units, the weight and volume of the fruit were very nearly equal for the first six months of growth, which in other words means that the specific gravity of the fruit taken as a whole is almost the same as that of water. After this period, the weight of the nut rapidly declined

until it becomes less than half the maximum value it had reached. This decline is in spite of the fact that the kernel goes on increasing in weight and the diminution in weight of the nut water is only a negligible fraction of the total loss in weight of the fruit. The obvious explanation is that the husk which is heavily soaked in water during the earlier stages of growth begins rapidly drying up even while the kernel is in the process of formation and undergoing active synthetic reactions. The volume of the fruit remains, however, constant but for the slight diminution that takes place owing to shrinkage as the fruit dries up.

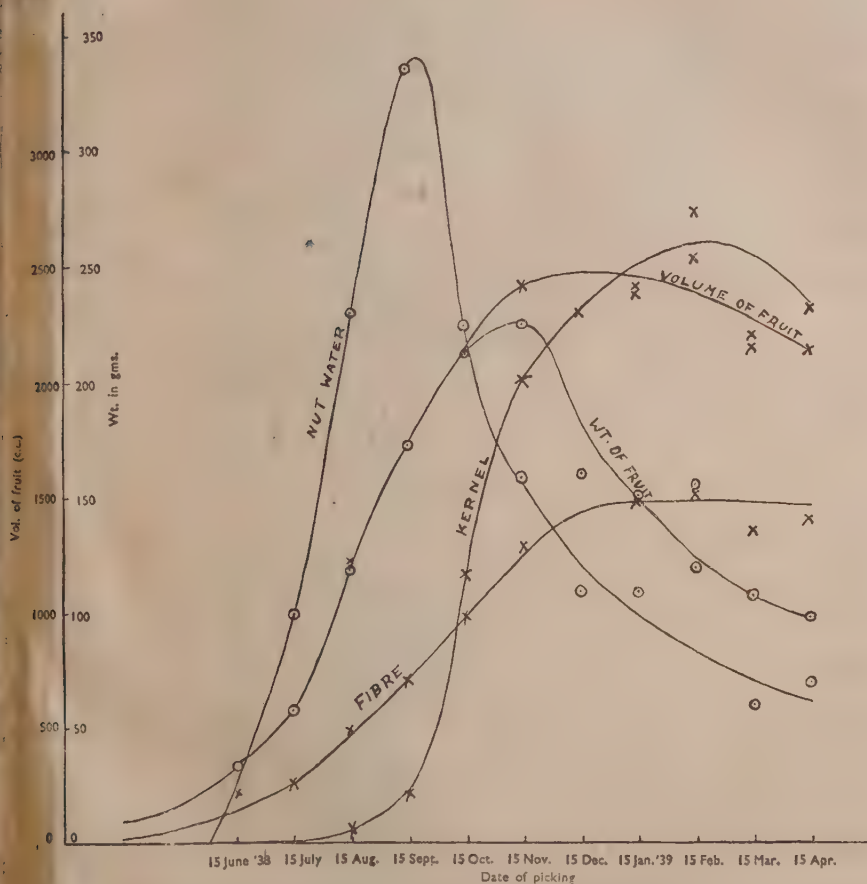


FIG. 1. Growth of fruit (Tree No. 171, Bunch No. 1)

TABLE I

Tree No. 171

Date of picking	No. of nuts in bunch	Weight of fruit (gm.)	Vol. of fruit (c.c.)	Vol. of nut water (c.c.)	Weight of kernel (gm.)	Weight of fibre (gm.)	Weight of pith (gm.)
<i>Bunch No. 1</i>							
15 June 1938	14	..	348	..	0	23	5
15 July " "	12	581	585	100	0	26	14
15 Aug. " "	11	1193	1230	230	7	50	31
15 Sept. " "	10	1720	1710	335	22	72	44
15 Oct. " "	9	2122	2150	225	117	98	46
15 Nov. " "	8	2250	2420	160	201	129	75
15 Dec. " "	7	1614	2300	110*	199	131	71
15 Jan. 1939	5	1515	2380	110	241	148	84
15 Feb. " "	4	1563	2530	120	272	151	103
15 March " "	3	1086	2145	66	219	134	92
15 Apr. " "	0*	984	2135	70	231	140	103
<i>Bunch No. 2</i>							
15 June 1938	9	..	1048	..	0	59	9
15 July " "	8	1699	1690	325	9	71	39
15 Aug. " "	7	2385	2450	293	120	98	59
15 Sept. " "	6	2457	2582	210	187	126	82
15 Oct. " "	5	2398	2680	195	246	163	93
15 Nov. " "	4	2063	2915	140	299	161	128
15 Dec. " "	3	1429	2590	95	262	149	106
15 Jan. 1939	2	1510	2760	125	284	172	113
15 Feb. " "	1	1263	2550	83	267	156	106

*Both the remaining nuts grew dead ripe and fell down before date; one of them was analysed and recorded as above

TABLE II

Tree No. 152

Date of picking	No. of nuts in bunch	Weight of fruit (gm.)	Vol. of fruit (c.c.)	Vol. of nut water (c.c.)	Weight of kernel (gm.)	Weight of fibre (gm.)	Weight of pith (gm.)
<i>Bunch No. 1</i>							
June 1938 .	12	..	623	..	0	35	11
July „ .	10	1122	1090	250	0	51	29
Aug. „ .	9	1600	1600	240	80	70	48
5 Sept. „ .	8	1567	1560	145	162	83	53
5 Oct. „ .	7	1625	1670	..	206	89	47
5 Nov. „ .	6	1480	1610	85	204	99	76
5 Dec. „ .	5	992	1525	40	211	96	52
5 Jan. 1939 .	4	895	1440	25	207	103	59
5 Feb. „ .	3	864	1585	60	187	106	68
5 March „ .	1	742	1640	30	222	118	83

Bunch No. 2

5 June 1938 .	12	..	316	..	0	21	7
5 July „ .	11	584	540	115	0	29	17
5 Aug. „ .	10	1129	1140	197	..	53	30
5 Sept. „ .	9	1367	1350	170	91	73	45
5 Oct. „ .	8	1562	1580	110	153	81	41
5 Nov. „ .	7	1621	1660	105	174	99	79
5 Dec. „ .	6	1245	1730	55	186	103	57
5 Jan. 1939 .	5	919	1520	55	172	100	59
5 Feb. „ .	4	931	1740	50	252	115	72
5 March „ .	3	765	1490	40	185	109	71

The two remaining nuts fell before 15th April 1939, after growing dead ripe

TABLE III
Tree No. 145

Date of picking	No. of nuts in bunch	Weight of fruit (gm.)	Vol. of fruit (c.c.)	Vol. of nut water (c.c.)	Weight of kernel (gm.)	Weight of fibre (gm.)	Weight of pith (gm.)
<i>Bunch No. 1</i>							
15 June 1938	8	..	238	..	0
15 July " "	7	604	590	135	0	28	15
15 Aug. " "	6	1400	1430	297	0	60	45
15 Sept. " "	5	1822	1860	335	34	89	53
15 Oct. " "	4	1942	1960	255	91	100	66
15 Nov. " "	3	1917	2035	180	143	110	107
15 Dec. " "	2	1797	2240	175	221	133	88
15 Jan. 1939	1	1522	2185	155	263	137	92
<i>Bunch No. 2</i>							
15 June 1938	8	..	138	..	0	9.4	1.5
15 July " "	7	368	340	65	0	18.5	11
15 Aug. " "	6	912	897	207	0	41	27
15 Sept. " "	5	1659	1700	345	6	82	52
15 Oct. " "	3	1823	1830	300	57	97	57
15 Nov. " "	2	1783	1845	180	139	104	87
15 Dec. " "	1	1907	2330	205	209	129	83

This branching of the weight-volume curve signals the beginning of a new series of chemical changes within the husk. It will be observed in Figs. 1 and 2 that the increase in weight of the fibre is almost uniform during the early period of growth, but the rate of growth declines after the weight of the fruit has begun to diminish. The reason for this may be that the formation of the non-lignin constituents of the husk comes to an end as soon as the husk begins to dry up, and that thereafter the increase in weight of the fibre content is only due to the lignification of the fibre, which proceeds more rapidly after the husk has begun to dry up. There is reason to suppose that the type of lignification that takes place after the drying up of the husk has commenced is significantly different from the type that precedes it. In the former, it is more a case of deposition of phenolic compounds on the cellulosic framework of the fibre than

of chemical linkage of the ring compounds with the chain-like structure of the cellulose. In this connection the author's conclusions based on the study of the nature of the lignin complex of coir fibre [Menon, 1936] may appear meaningful. Table IV shows that the lignin value of the fibre goes on steadily increasing practically to the very last stages of growth of the fruit. This is in agreement with a previous observation of the writer [Menon, 1935] that the methoxyl value of coir fibre increases with the growth. Table V shows the quantity of non-lignin present in the fibrous matter of the fruit at the various stages of growth. Up to November 1938, the non-lignin content steadily increased, but the figures obtained for the next five months do not indicate, making due allowance for individual variation of nuts, that it increased subsequently. The practical significance of this observation is considerable. It proves that in picking the nuts before they are fully ripe, not only no loss in yield of fibre results unlike in the case of copra, but there is the striking advantage of obtaining a cleaner and whiter fibre that registers a higher non-lignin value and a lower lignin value. The advantage regarding colour and gloss is vital. The discoloration that the fibre is subjected to as the drying of the husk becomes intense and the extraneous lignin matter of the husk deposits itself on the fibres, is permanent and ineradicable; it is responsible for the very low prices obtained for such fibres in the market. The practice adopted, therefore, in Malabar of picking the nuts while they are still green, is scientifically justified from the view-point of coir production.

TABLE IV

Analysis of coir fibre extracted from nuts of varying growth

(Palm No. 171, bunch No. 1)

Date of picking	Age in months*	Moisture (per cent)	Specific gravity	Lignin (per cent)	Furfural (per cent)
June 1938 . . .	X	10.0	1.52	28.0	16.5
July „ . . .	X+1	8.9	1.52	27.4	16.0
5 Aug. „ . . .	X+2	10.0	1.50	31.1	15.5
5 Sept. „ . . .	X+3	9.3	1.50	32.1	..
5 Oct. „ . . .	X+4	10.0	1.50	34.1	..
5 Nov. „ . . .	X+5	10.3	1.51	34.4	14.3
5 Dec. „ . . .	X+6	9.7	1.50	34.3	..
5 Jan. 1939 . . .	X+7	..	1.49	35.5	..
5 Feb. „ . . .	X+8	9.6	1.48	36.4	14.4
March „ . . .	X+9	11.3	1.48	36.0	..
Apr. „ . . .	X+10	..	1.49	37.2	..

*The value of X, as read from the graphs, is about 1 1/2—2 1/2 months

TABLE V
Variation of the non-lignin content of coir fibre with growth

Date of picking	Weight of fibre gm. (W)	Lignin per cent (x)	Non-lignin per cent (100-x)	Weight of non-lignin in fibres $\frac{W(100-x)}{100}$ gr.
15 June 1938	23	28.0	72.0	16.6
15 July „	26	27.4	72.6	18.9
15 Aug. „	50	31.1	68.9	34.5
15 Sept. „	72	32.1	67.9	48.9
15 Oct. „	98	34.1	65.9	64.6
15 Nov. „	129	34.4	65.6	84.6
15 Dec. „	131	34.3	65.7	86.1
15 Jan. 1939	148	35.5	64.5	95.5
15 Feb. „	151	36.4	63.6	96.1
15 March „	134	36.0	64.0	85.8
15 Apr. „	140	37.2	62.8	87.9

Another remarkable fact revealed by Table IV is that the specific gravity of the fibre during its growth undergoes a little alteration, but this alteration is surprisingly on the negative side. This may be of great theoretical significance, inasmuch as the process of increasing lignification is not only not attended by any increase in specific gravity of the lignified material, but attended by a perceptible diminution of the same.

The furfural value of the fibre too diminishes by slight degrees during its growth. Making allowance for the increasing proportion of lignin in the fibre, this indicates that the cellulosic portion of coir fibre is very rich in furfural-yielding substances from the very beginning. The proportion of such substances in the cellulose remains practically undiminished to the very end.

One fact remains to be mentioned regarding the husk of the coconut. The non-fibrous constituent of the husk, as has already been stated, was separated from the fibres by preliminary boiling with dilute sodium sulphite solution. The reaction that takes place is not quite clear, but it is found to be very effective in treating coconut husk during all stages of growth. The non-fibrous matter isolated from the immature nuts was not a corky powder as is commonly obtained from mature coconuts but a fine sticky paste which on drying assumed a leathery consistency. This paste was capable of binding the fibres into a tough mat. Elaborate experiments were recently conducted on this subject

showed by large-scale trials at the Forest Research Institute, Dehra Dun, and a patented process has been perfected for the manufacture of a variety of use-articles, now styled as 'Menonite' products, from the entire husk of immature coconuts naturally falling from the tree and obtained as an agricultural waste in coconut plantations.

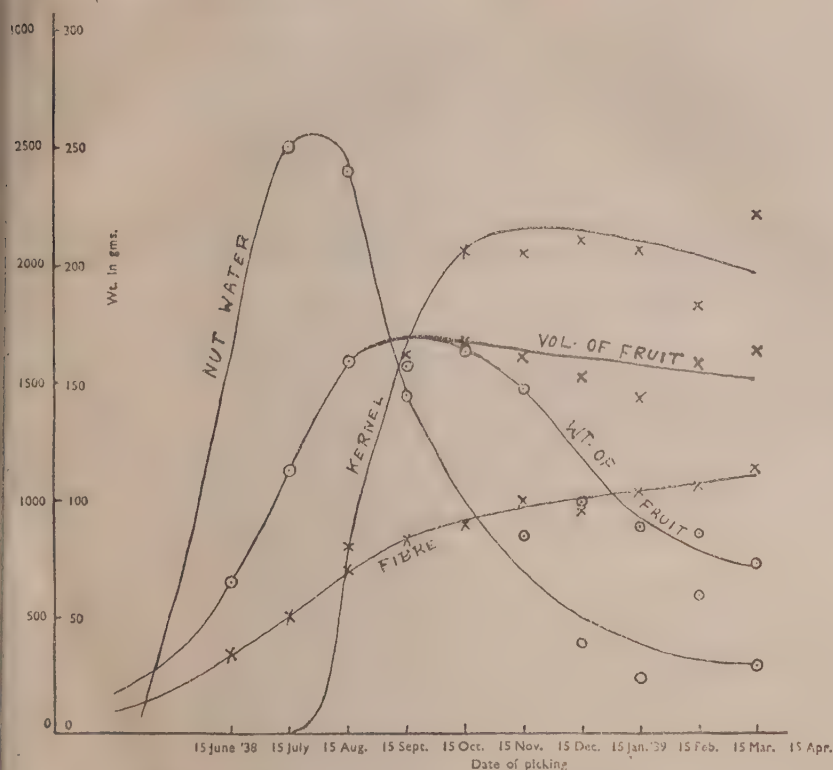


FIG. 2. Growth of fruit (Tree No. 152, Bunch No. 1)

Passing on to the remaining constituents of the coconut, Figs. 1 and 2 reveal several interesting features. The kernel is the last constituent to begin formation, and from the interpolated curves it is found that its formation does not commence during the first three or four months. Once it commences formation, its growth is of a 'blitz' nature for the first two or three months, during which time it gathers most of its raw material. Afterwards growth in the form of weight slackens, the kernel thickens and increases in density, and the formation of fat becomes vigorous. Ultimately, as the moisture content of the kernel falls, its gross weight also registers a decline. An analysis of the kernel at various stages of growth, similar to the one conducted in the case of coconut husk, was not carried out, as the author is exclusively confined to work on coconut husk. But there is ample evidence to conclude that the fat content of the kernel goes on increasing to the last days of growth of the fruit,

and that from the view-point of the oil industry the nuts are most advantageously gathered as late as possible. There is thus a conflict between the interests of the oil and coir industries. A compromise is the result, as practised in Malabar and the Southern Province of Ceylon, where the nuts are picked before they are fully ripe.

SUMMARY

Certain changes undergone by the various components of the coconut fruit during its growth from infancy to maturity have been traced by means of experiments performed over a period of about a year on select bunches of three different trees.

ACKNOWLEDGEMENT

Thanks are due to the Board of Management and the Director of Research of the Coconut Research Station of Ceylon for the grant of estate and laboratory facilities.

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THE NATURE OF REACTIONS RESPONSIBLE FOR SOIL ACIDITY*

IX. THE ACID CHARACTER OF HYDROGEN CLAY

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(With nine text-figures)

THE present paper is the concluding part of this series and gives a connected account of the experimental work relating to the acid character of hydrogen clay done in this laboratory. Theoretical considerations underlying this work have been discussed in an earlier paper [Mukherjee, Mitra and Mukherjee, 1947] and details will be avoided. It is, however, felt that a brief historical outline of the development on the theoretical side will be useful at this stage. The authors have not come across a comprehensive publication dealing with this aspect. Modifications of the current theoretical treatments are called for in the light of recent researches in this and other laboratories and it is intended to publish elsewhere a paper on these aspects.

THE PHYSICAL AND CHEMICAL CONSTITUTION OF HYDROGEN CLAYS

The expression 'soil acidity' has been used to indicate, somewhat contrary to usage, the inherent acid character of soils. The nature and amount of the clay fraction determine to a large extent many of the properties of the soil, including its acid character. The hydrogen clay obtained from a soil represents the acid material in the clay fraction. From the point of view of physical and chemical constitution this clay fraction is a rather complex system. It consists of several chemical components in the sense of the phase rule some of which are not yet well defined and of particles whose size distribution varies widely from one clay to another. Their dimensions range from 2μ down to the lower limits of the colloidal range and the assemblage manifests colloidal properties.

Following the classical researches of van Bemmelen [1912] the inorganic colloidal material of the soil has often been regarded as a mixed gel of the oxides of iron, aluminium and silicon (also of manganese and titanium in much

*Most of the results given in this series of papers have been taken from the Annual Reports for the years 1935-40 on the working of a scheme of research into the 'Properties of Colloid Soil Constituents' financed by the Imperial Council of Agricultural Research, India.

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smaller quantities); and the applications of the principles of colloid science the study of soils has led to a rapid progress of our scientific knowledge regarding them. For a long time, however, this 'mixed gel' hypothesis and erroneous stress on some aspects of colloidal properties appear to have kept the background the crystalline nature of the inorganic soil colloids now definitely established by X-ray [Hendricks and Fry, 1930; Kelley, Dore and Brown, 1931; Hofmann, Endell and Wilm, 1934; Nagelschmidt, 1933] optical [Marshall, 1930, 1935; Hendricks and Fry, 1930] and thermal [Kell, Jenny and Brown, 1936] investigations. Moreover, synthetic mixtures purified colloidal oxides of silicon, iron and aluminium appear to differ materially from the clays obtained from soils [Bradfield, 1923].

Modern researches make it increasingly clear that the basis of a unitary treatment of the properties of the soil and clay lies in the recognition that they are essentially disperse systems with a dominant electrochemical (polydispersed) character. Their colloid constituents belong to the class of electrolytic colloids.*

The clay fraction as also the coarser particles which together build the inorganic material of the soil are formed by the weathering of rocks which are polar or electrolytic substances. And the chemical reactions involved in weathering are mainly of an electrochemical character in which hydrolysis plays an important part. The influences controlling this hydrolysis, such as the reaction of the medium (pH), the salt content, time of contact, degree of leaching and others are largely conditioned by climatic factors, e.g. rainfall, temperature and their seasonal variations. The weathered product is also essentially polar in character and carries with it the impress of the physical and chemical reactions which the parent rock has undergone. It is therefore not surprising that the importance of rather detailed investigations by physical and chemical methods of the colloid constituents of soil in soil genesis and classification is being increasingly realised [Byers *et al.*, 1931, 1932, 1933, 1936; Edelman, 1939].

In soils and clays the absorption complex consisting of the secondary minerals, comminuted primary minerals, humus and the free oxides is considered to be responsible for most of the colloidal properties manifested by them. Base exchange, flocculation, deflocculation, soil structure, shrinkage and swelling are illustrations of such properties which are determined by the nature and amount of the 'complex' present in the soil. The hydrogen clay represents the acid form of the complex freed from exchangeable bases. It is the acid part which mainly determines the colloid behaviour of soil. When freed from organic matter, it represents the acid form of the inorganic part of the complex. It would thus appear that the electrochemistry of the colloid constituents, the clay and humus fractions of the soil, is of direct interest in the elucidation of many aspects of soil behaviour. And investigations on the electrochemical properties of the colloidal acid, the hydrogen clay, occupy a central place in a systematic treatment of soil behaviour.

*The expression 'colloidal electrolytes' should in our opinion be used exclusively for those electrolytic colloid systems where there is a thermodynamic equilibrium between the polymers and monomers. The expression 'electrolytic colloids' should be used more generally so as to include, in addition to the above, colloidal systems where there is no such equilibrium but which show pronounced electrolytic properties.

The distinguishing characteristic of an acid is its power to combine with or to donate a proton to an acceptor. Colloidal acids and their salts have the additional characteristic of base exchange—a property which is not confined to soils, clays and other silicate minerals (e.g. bentonites, zeolites) and artificially prepared silicates (e.g. permutite) but is also exhibited by such organic substances as the acidic complexes of gums, resins and proteins.

Apart from base exchange these substances which differ so widely in their chemical composition and constitution show a number of points of resemblance. Their acidic part as has been previously indicated is complex and has to be regarded as an anion of macro-dimensions. It carries a negative charge and has the general characteristics of typical negatively charged colloids of which it constitutes a special class distinguished by their stability and the large number of easily displaceable or reactive electrolytic ions associated per gramme of the material. The connecting link in the study of their common characteristics is consequently the fact that they are electrolytic colloids of an acidic nature with an electrical double layer surrounding their particles. The existence of such a double layer was postulated by Quincke and a picture of the electrical conditions inside the double layer was given by Helmholtz. Gouy (1910) formulated the existence of an atmosphere of diffuse ions which was in essence implied in Helmholtz's mathematical treatment. The manner in which the electrical double layer is built up and the nature and distribution of the carriers of the electric charges which determine to a very large extent the behaviour of these systems have been set forth in detail by one of us [Mukherjee, 1921; 1922]. The recognition of the part played by the electrical double layer and by the ions constituting it has, however, come about gradually (further discussed later on).

THEORIES OF BASE EXCHANGE

The history of the development of our knowledge of hydrogen clays is closely associated with the study of base exchange. It will be shown later that the interaction between a hydrogen clay and an electrolyte mainly consists in an exchange of H ions associated with the hydrogen clay for the cations of the electrolyte. Base exchange studies have thus an important bearing on the properties of hydrogen clays. Earlier work on base exchange was, as the name of the topic suggests, concerned with the exchange of cations other than hydrogen ions. Exchange of the latter has come to be recognized more recently and systematic work is mainly associated with studies of hydrogen clays.

Way [1850] appears to have considered base exchange as an action involving double decomposition. Since Way, several attempts have been made to formulate this reaction on the basis of the law of mass action. Gaus [1905] found that a permutite having the composition $\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot n\text{H}_2\text{O}$ rapidly takes up its alkali metal in exchange for an equivalent quantity of another ion on being washed with its salt. The exchange was considered by him to be governed by the mass action equation $K = \frac{x^2}{(m-n-x)(g-x)}$ where K is the equilibrium constant; m , the amount in grammes of the exchange complex; n , the total amount in mols of exchangeable cations in the complex; g , the total amount of the displacing ion in solution and x , the amount of it taken up by

base exchange. Rothmund and Kornfeld [1918] suggested the more general mass law equation $\frac{x}{m} = K \frac{C_1^{a_1} C_2^{a_2}}{C_1^{b_1} C_2^{b_2}}$ where C_1 and C_2 are the concentrations of two ions in the solid phase and C_1' and C_2' are the corresponding concentrations in the liquid, it being assumed that the added cation forms an isomorphous mixture with the solid so that there is only one solid phase. The general equation is in harmony with the observation often made (Wiegner and Mui [1919]) that the equilibrium is independent of the volume of the solution long as the total amount of the displacing cation contained in it is constant. Equations based on the mass action principle have also been set up by others by Anderegg and Lutz [1928], Kerr [1928] and Vanselow [1932] under various simplifying assumptions. Marshall and Gupta [1933] have critically examined these equations and have shown that the equilibrium constant calculated from them has different values.

Further complications are met with when adsorption on the surface reactions in colloidal systems have to be considered. Linder and Pic [1895] and Whitney and Ober [1901] observed that in the coagulation of colloidal solutions of arsenious sulphide by barium chloride, barium ions carried down by the coagula. It has been shown more recently by Rabinowitz [1915] and Weiser and Gray [1931] that hydrogen ions surrounding the colloidal particles are exchanged. Neither this exchange, nor its significance, noticed for a long time. Van Bemmelen [1912] extensively studied adsorption of electrolytes by precipitates, e.g. of those of importance in chemical analysis. Lottermoser and Reche [1908] in their well-known studies on silver salts noted such adsorption. Mare [1911; 1913] came to the conclusion that adsorption of an ion by an insoluble polar solid, although weak, is of general occurrence when the ion can form an isomorphous and insoluble substance with one of the constituent ions of the solid (Fajans and Beckwith, 1916; Mukherjee and Basu, 1927). An exchange adsorption or displacement adsorption gradually came to be recognized. Wiegner [1912] found that the exchange could in most cases be represented by Freundlich's equation $\frac{x}{m} = KC^{1/p}$ where m is the amount of the adsorbent in gramme; x , the amount adsorbed; C , the equilibrium concentration, and K and p are constants. Jenny's [1932] modified equation $\frac{x}{m} = K \left(\frac{C}{C_0} \right)^{1/p}$ takes account of the fact that the exchange is often independent of dilution; C_0 , in this equation, represents the initial concentration of the added salt. None of these parabolic equations, however, can explain the observation that at high concentrations of the added salt the exchange reaches a maximum. To meet this difficulty, Vageler [1934] proposed the hyperbolic equation $Y = \frac{XS}{S+C}$ where Y is the amount taken up per gramme of the substance; X , the number of equivalents of the cation added per gramme of the adsorbent; S , the maximum exchange capacity; C , the number of equivalents of the added cation for which 50 per cent S is exchanged. The Vageler equation agrees better at high concentrations with experimental results than the Wiegner equation. All these equations, however, are rather empirical and the various constants involved in them have little physical significance.

Jenny [1936] has recently suggested a simple base exchange model with the aid of which he has derived an equation based on statistical considerations.

has considered a plane surface having a definite number of attraction spots per unit area. If the ions, atoms or molecules initially adsorbed on these spots are designated as b and the exchanging bodies as w then at equilibrium the number of w bodies adsorbed or released is given by the equation
$$\frac{(S+N) \pm \sqrt{(S+N)^2 - 4 S_w N_w (1-V_w/V_b)}}{2 (1-V_w/V_b)}$$
 where N is the amount of electrolyte (number of ions) initially added; S , the saturation capacity; and V_w and V_b , the volumes of the oscillating spaces of the w and b bodies. The latter volumes are characteristic of the exchanging and exchanged bodies; and exchange adsorption takes place whenever the w 's slip in between the surface and the space occupied by the b 's which execute to and fro motions between the surface and a mean position in the bulk of the liquid. An almost perfect agreement between theory and experiment was observed by Jenny in certain cases while in others, systematic deviations occurred. Jenny sought to explain these latter on the basis of the structural peculiarities of the colloidal particles (discussed below) and the nature of the exchanging ions. Difficulties were encountered when hydrogen ions were involved and when the two ions participating in the exchange had widely different properties.

Further complications have been observed by later workers. For instance, Renold [1936] found a marked difference in the base exchange property of a permutite having the same composition and proportion of two exchangeable cations but prepared in different ways. Thus a mixed or 'hetero-ionic' permutite of given composition, e.g. one saturated with a fixed proportion of K and Ba ions can be obtained starting from either of two homo-ionic permutites saturated only with K or Ba ions. Renold [1936] observed that if the mixed permutite was obtained from the K -permutite its exchangeable K was more difficult to displace by a third cation than if it was prepared from a Ba -permutite.

The recognition of the part played by the electrical double layer in base exchange reactions, especially of soils and clays, originates from the work of Mukherjee [1922], Hissink [1924-25] and notably Wiegner [1925]. According to Wiegner, colloidal clay is made up of micelles consisting of an inner kernel which is an ultramicon, an inner layer of anions fixed on the surface and an outer swarm of cations. These cations can be displaced by others and the ease of displacement depends on the valency and radius (together with the hydration envelope) of the displacing cation and on the nature and the intensity of the force of attraction between the inner layer of anions and the cations already existing in the double layer. The replacing powers of different cations are given by their so-called 'symmetry values' which represent the 'ionic exchange in percentage when the number of ions added to the system is made equal to the total number of exchangeable ions in the colloidal complex'. Wiegner's fundamental ideas have since been extended by Jenny [1932], Marshall and Gupta [1933], Pallmann [1938] and others. The picture, however, is not yet complete in all its details. According to the views on the origin of the double layer formulated by one of us [Mukherjee, 1922] the base exchange clays have a layer of electrolytic ions, mainly anions,* built up on the surface of their particle by lattice forces which constitute a primary

*If the clay is amphoteric the primarily adsorbed layer will consist of both cations and anions.

layer of adsorbed ions; an equivalent amount of oppositely charged ion (here, cations) remains associated with each particle partly as a fixed secondary layer and partly as 'mobile' osmotically active ions*. In the interaction with an electrolyte, the cations, fixed and mobile, already present in the double layer are liable to be exchanged for those of the electrolyte. The displacing power of different cations would depend on their valency and mobility, if the adsorption was the result of simple electrostatic forces alone [Mukherjee, 1922]

SOME ASPECTS OF THE ACID CHARACTER OF SOIL

A quantitative formulation of the acid character of soil which, as stated before, is the main connecting theme in the electrochemistry of soil has long been lacking. The nature of the interaction between soil and neutral salts in which acid is liberated has been a subject of controversies. The main weakness of the purely chemical explanation according to which the reaction is simple double decomposition process [Way, 1850; Truog, 1916; Page, 1922] lies in the assumption that the soil acid has to be considered to be unusually strong as, otherwise, it would not decompose a neutral salt combining with the base and liberating the strongest known acids, e.g. hydrochloric acid. Such an acid is evidently unknown and it is difficult to conceive of such reaction. On the other hand, the principal drawback of the purely physical explanation [Hopkins, 1903; Cameron, 1910; Parker, 1913] is that it links up the free energy of the process with an ill-defined surface energy term.

The theory of the double layer, on the other hand provides a more rational and simple explanation. According to the picture suggested by one of us [Mukherjee, 1922], 'an extract with a neutral salt can be acid when the cations displaced from the second sheet of the double layer contain hydrogen ions. Hissink [1924] also considered that hydrogen ions occur together with Na^+ , Ca^{++} and Mg^{++} ions in the outside sheet of the double layer. The H^+ ions are also exchangeable. When we treat a soil with a solution of KCl the filtrate contains H^+ ions. The following reaction takes place:—



Though the rôle of the double layer is now fairly generally realized, the above simple picture cannot explain several features. Thus, neutral salt extracts of acid soils almost always contain aluminium ions [Daikuhara, 1914]. Opinion differs as to whether Al ions are present in the outer sheets of the double layers and are directly exchanged for the cations of the salt, or whether they are liberated by a process of secondary dissolution of a part of the aluminosilicate base exchange complex or the free alumina contained in it by the acid set free consequent on the exchange of the H^+ ions of the double layer for the cations of the salt. Another observation which is not easy to understand is that an acid soil does not show a neutral reaction even on continued leaching with a solution of a neutral salt [Hissink, 1924-25]. Indeed, such difficulties led Hissink [1935] to remark that no existing theory

*A distinction between fixed and mobile ions in the outer sheet of the double layer has not been made by Wiegner. This distinction is justified by results of investigations on hydrogen clays discussed later.

an adequately explain the nature of the interaction between an acid soil and neutral salt.

The nature of the acid-base interaction in soil cannot also be said to have been fully understood. There is much confusion regarding the part that the titration of the base plays in this interaction. Titration curves with different bases can rarely be superimposed and different amounts of these bases are required to attain a certain pH [Hissink and van der Spek, 1925; Oakley, 1927]. *Ad hoc* assumptions regarding the differences in the solubility of the salts which the soil acid forms with different bases have been made [Truog, 1916; Joseph, 1924; Oakley, 1927] to explain this non-equivalence, it being even necessary to postulate a wholesale existence of insoluble salts of alkali metals. Another observation for which an adequate explanation has not been forthcoming is that more base is necessary to attain a certain pH when the soil is titrated in the presence of a neutral salt than when titrated with the base alone [Crowther and Martin, 1925; Hardy and Lewis, 1929; Clark and Collins, 1930]. The soil buffer action is in fact an extremely complicated expression of several types of reactions in which anions (molecularly dispersed anions, e.g. HCO'_3 and HPO''_4 and macro-anions such as those of humus and the so-called zeolitic complex ions) and cations (e.g. Al^{+++} and Fe^{+++} ions) of a number of weak acids and bases take part. A buffer action although comparatively much weaker may be shown by the free inorganic oxides contained in the soil. Further, the possibility of a total absorption of the base as suggested by Oakley [1927] and Mattson [1931] cannot be altogether ignored. A quantitative formulation of the soil buffer action comprehending at least the chief factors has not been forthcoming. The gaps in our basic knowledge of the subject have been responsible for the element of arbitrariness in the various routine methods in vogue for estimating the so-called lime requirement and the base exchange or base-binding capacity of soil. These methods seldom give concordant results (further discussed later). Unlike the estimation of acids in true solution, or colloidal systems in which the different phases and components taking part in the interaction can be clearly defined [Mukherjee, 1922; 1929], the amounts of acids estimated by these methods are usually ill-defined and there is often no clear idea as to what is being estimated by a particular method.

THE SCOPE AND OBJECT OF THIS WORK

Considerable light has been thrown in recent years on problems of soil acidity by investigations (discussed more fully later) on hydrogen clays and systems resembling them carried out, among others, by Wiegner and associates at Zurich, Anderson, Brown and Bayer in America, Mattson at Upsala, Marshall in England, Hissink and coworkers and Edelman and associates in Holland. Definite and adequate information, however, is still lacking on several fundamental points (mentioned below). Our work aims to secure this information. Specially oriented technical procedures, described in the previous parts of this series (see, in particular, part IV [Mukherjee *et al.*, 1936]; part V [Mitra 1936]; and part VII [Mitra, 1940], have been used which have yielded more accurate results than are usually aimed at in soil investigations. Also, the problems have been approached from a point of view which differs from previous investigations of a similar nature. Instead of studying

only the properties of hydrogen clays, simpler but similar systems which are amenable to straightforward theoretical treatment have been examined. They were expected, on theoretical grounds, to be more suitable for the study of the processes underlying the interaction of hydrogen clay with electrolytes. The main objective of the work on hydrogen clay has been the elucidation of the following topics :

- (1) The electrochemical character of hydrogen clay ;
- (2) the manner in which this electrochemical character varies : (a) with the nature of the soil from which the hydrogen clay has been isolated, (b) with the particle size of the hydrogen clay, and (c) on the removal of the silica and sesquioxides contained in the hydrogen clay ;
- (3) the base exchange capacity of hydrogen clay and the factors which it depends ; and
- (4) the weathering process.

The work on hydrogen clays is being now extended to sub-fractions of hydrogen clays, clay minerals of standard purity and the so-called clay minerals and these latter investigations will be dealt with in separate series of papers.

Modern electrochemistry gives in terms of the concepts of activity coefficient and ionic strength a satisfactory representation of the interaction between an acid and a base barring complications arising out of other types of chemical reactions which have of course to be taken into account. In order therefore, to understand the nature of hydrogen clay, it was considered necessary, firstly to ascertain how far its behaviour can be brought within the compass of our current concepts of electrochemistry ; secondly, to ascertain features, if any, which show that they have properties which cannot be comprehended by these concepts ; and thirdly, to formulate a picture which would enable us to understand these special characteristics and reconcile them with the usual concepts.

The properties of so complex and variable a system as the hydrogen clay can be properly understood only by systematic studies of hydrogen clay obtained from a sufficiently large number of different types of soils. Those used for this work were obtained from different parts of the country (details given in Table I) and had widely different mechanical and chemical compositions and base exchange properties. The results summarized in this paper show that in spite of these variations, the hydrogen clays and sub-fractions of hydrogen clay obtained from them reveal a number of important common features though individual differences are not lacking. The present paper is mainly concerned with the common features. Individual differences have also been indicated ; they have been more fully discussed in part VII [Mukherjee, Mitra *et al.*, 1942].

EXPERIMENTAL

Details regarding the method of preparation of the hydrogen clays, experimental arrangements and procedure have been given in parts IV, V and VI. The following soils and bentonites** were used.

* i. e. clays with exchangeable cations other than H^+ ions

**Bentonites usually have chemical composition and base exchange properties similar to those of soil. The samples of bentonite used for this work were kindly supplied by the Assam Oil Company

TABLE I

Particulars of soils, bentonites, hydrogen clays and hydrogen bentonites used

Lab. No.	Description of soil or bentonite	Silica : sesquioxide ratio (molar) of entire clay fraction	Ref. No. of corres- ponding hydrogen clay or hydrogen bentonite
13	Brownish yellow soil (unmanured) from Government Farm, Suri (Bengal) collected at a depth of 6-12 in. from Agricultural Chemist's experimental plot, block A 1-16, plot Nos. 3, 5, 16	2.34	E
14	High land acid soil from Government Farm, Burdwan (Bengal), collected at a depth of 0-6 in. from block B, plot No. 40 of the Farm	1.94	F
20	Neutral calcareous soil (brown loam) from Government Seed Farm, Kalyanpore (U.P.), collected at a depth of 0-6 in.	2.10	H
25	Black cotton soil (neutral, calcareous) from Satara (Bombay), collected at a depth of 0-6 in.	2.50	I
32	Neutral black soil from Bilaspur, near Raipur (C. P.), collected at a depth of 0-6 in.	2.54	K
22	Red laterite soil (acidic) from Government Farm at Dacca (Bengal) collected at a depth of 0-6 in.	1.99	L
34	Black soil from Government Farm, Akola (Berar), collected from a depth of 0-9 in.	2.19	M
33	Bhata red laterite soil from Raipur (C. P.), collected at a depth of 0-6 in.	1.88	N
46	Non-lateritic black calcareous soil (B-type) from Government Farm at Padegaon (Nira, Poona), collected at a depth of 0-12 in.	2.51	Padegaon-B
51	Acid soil from Government Farm at Jorhat (Assam), collected at a depth of 0-6 in.	2.58	Jorhat-F
53	High land acid soil on old alluvium from Government Farm at Latekujan (Assam), collected at a depth of 0-6 in.	2.47	Latekujan-F
B. O. C. 1	Bentonite from Hati-Ki-Dhani	2.86	Hati-Ki-Dhani-B
B. O. C. 3	Bentonite from Bhadres	2.90	Bhadres-B

RESULTS

Colloidal solutions of hydrogen clay as heterogeneous acid systems.

The interpretation of the electrochemical properties, especially the titration curves, of an acid system would largely depend on whether the system is single, or polyphase system. Colloidal solutions of hydrogen clays have often been regarded as homogeneous acid systems. Bradfield [1923 ; 1927] and Bayer [1930] have attributed to them a weak monobasic acid character from a study of their titration curves. The so-called 'suspension effect' of Wiegner and Pallmann [1929] according to which a suspension of an insoluble acidic substance, e.g. a hydrogen clay, has a much higher H ion activity than the pure dispersion medium indicates, on the other hand, a polyphase character of such an acid system. Doubts have recently been expressed regarding the validity of the suspension effect [Rabinowitsch and Kargin, 1935]. Experiments carried out during the past few years in this laboratory with carefully purified colloidal solutions of hydrogen clays fully bear out this effect.

Some results are given in Table II.

TABLE II

Free and total acids of hydrogen clay sols and their ultrafiltrates

Sol	pH	Free acid H-ion conc. \times $10^5 N$	Total acid* $\times 10^5 N$
E	4.66	2.19	24.3
Ultrafiltrate	6.10	0.08	Nil
F	4.41	3.89	38.0
Ultrafiltrate	5.90	0.13	Nil
G	4.57	2.69	40.0
Ultrafiltrate	5.85	0.14	**
H	4.52	3.02	99.0
Ultrafiltrate	6.05	0.09	**

*The total acidities have been calculated from the inflexion points in the potentiometric titration curves of the sols with baryta. It will be shown later that this value does not denote the concentration of the total neutralizable acid as the added base continues to react beyond the inflexion point.

**Not determined

The ultrafiltrates of the sols are practically free from any acid, while the sols have a fairly low pH. The existence of mobile hydrogen ions giving rise to pH's of the order of 4.5 is, therefore, beyond doubt.

The special features of some simple polyphase acid systems: Difficulties of their interpretation in the light of the classical concepts

Reference has already been made to the extremely complex nature of hydrogen clay as a chemical entity and as an acid system. For a proper understanding of its properties investigations on simple polyphase systems, e.g. colloidal silica, alumina, and palmitic and stearic acids have been carried out and the results discussed in parts I, II, III and IV [Mukherjee *et al.*, 1931 ; 1932].

1934; 1936] and in other publications [Mukherjee, Mitra and Mukherjee, 1937; Mukherjee, 1937; Dutta 1939; Chatterjee 1939]. These investigations have served a twofold purpose. They have brought to light a number of characteristic features of heterogeneous acid systems which are foreign to the concepts of classical electrochemistry; secondly, they have served as a guide to the investigations on hydrogen clay. A connected account of a part of the work on the simple systems has been given by Mukherjee, Mitra and Mukherjee [1937]. The following is a summary of the more important observations which have a direct bearing on the work on hydrogen clay discussed in this paper.

A simple heterogeneous acid system where the part played by the solid phase can be readily understood is illustrated by the mixture of a solid acid and its saturated solution. Fig. 1 reproduced from part I gives the titration curves of saturated solutions of cinnamic acid in presence (curves 2 and 3) and absence (curve 1) of the solid acid.

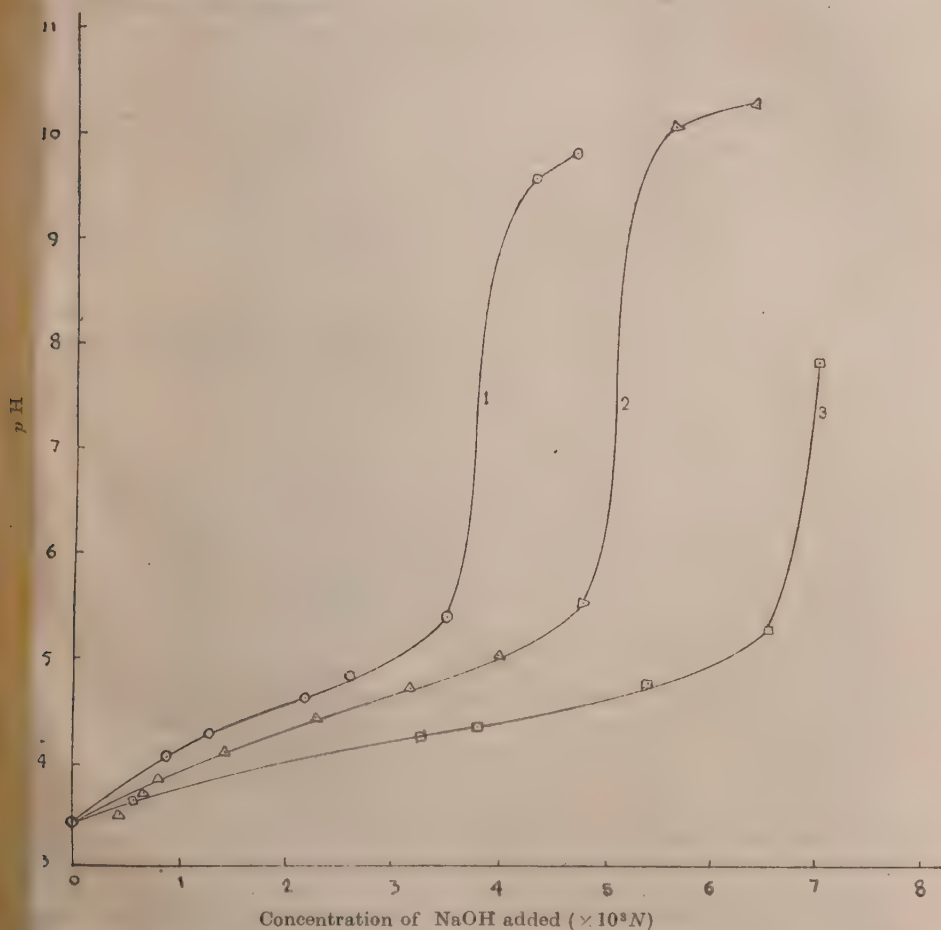


FIG 1. Titration curves of saturated solutions of cinnamic acid in the presence and absence of excess solid acid

The amount of the acid reacting with the base (NaOH) increases so long as solid cinnamic acid is present. The resulting salt, sodium cinnamate, remains in solution. The equilibrium pH on the addition of a definite amount of the base can be calculated from the volume of the aqueous phase and the solubility and dissociation constant of cinnamic acid. The actual pH during the course of the titration, i.e. the form of the titration curve, is, however, determined not merely by these equilibrium values but by the kinetics of the interaction between the solid acid and the base. The net effect of the presence of the solid phase is a prolongation of the initial portion of the titration curve (Fig. 1, curves 2 and 3) where the pH does not change so rapidly as it does in the case of the saturated solution containing no solid acid (Fig. 1, curve 1). The initial portion of the curve thus resembles that of a stronger acid. As opposed to a strong acid in true solution, however, the influence of increasing concentrations of the salt in suppressing the dissociation of the acid manifests itself in the region of higher pH values. When the solid phase disappears the titration curve resembles, subject to the influence of the higher anion concentration, that of the saturated solution. If, however, one attempts to calculate the dissociation constant from different points of curves 2 and 3 using the well-known Henderson equation, constant values are not obtained. This arises from the fact that the fundamental assumption underlying the derivation of the equation that the whole amount of the reacting acid exists in true solution is not satisfied when the solid phase is present. The variability of the total acid under this latter condition leads to values of the dissociation constant thus calculated which are fictitious and denote quantities which have not the usual significance.

If a colloidal solution of a hydrogen clay were an acid system which gave two insoluble solid phases — a solid acid and a solid salt, its behaviour as deduced from classical considerations would be represented by the titration curves of palmitic and stearic acid sols [Mukherjee, 1937; Iyer, 1932; Datta, 1939]. The titration curve of a stearic acid sol with baryta is reproduced from Datta's paper (Fig. 2).

The curve shows an initial rise, then a middle horizontal portion at a practically constant pH between 6.2 and 6.3 followed by a sharp inflexion. These features can be explained by the phase rule. Barium stearate is insoluble in water. On the addition of barium hydroxide the pH rises till the solubility product of barium stearate is reached. So long as the insoluble salt separates out as a second solid phase, the system which has three components (barium hydroxide, stearic acid and water) and exists in four phases (the solid acid, the solid salt, the liquid and the vapour) is univariant. At constant temperature, therefore, the liquid phase should have a constant composition. The horizontal portion of the curve confirms this expectation. When the solid acid phase has disappeared the system becomes bivariant and consequently the pH shoots up on further addition of the base. During the titration with baryta, the barium stearate molecules continually split off from the surface and form a crystal lattice of their own. Inner layers are therefore, continually exposed to the action of the alkali and ultimately the whole of the acid takes part in the reaction. The total acid at the inflexion point has been found to agree with the amount of acid in the sol estimated on extraction with ether.

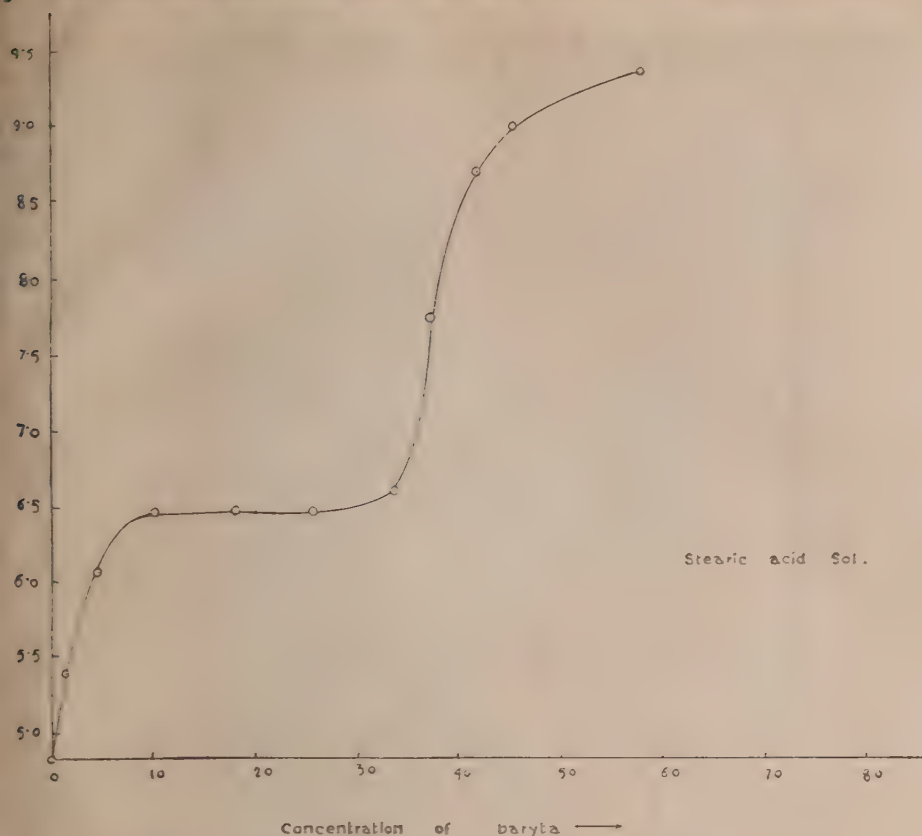


Fig. 2. Titration curve of a stearic acid sol with baryta

The above simple heterogeneous acids have the advantage that the nature of the surface reactions can be visualized and the amount of the acid solid phase entering into the reaction can be calculated when equilibrium has been established. In most colloidal solutions of acidic substances, however, we have no *a priori* knowledge of the quantities necessary for the calculation, namely the solubility, the anion concentration and the dissociation constants. In the case of an acid in the dissolved condition, the cations and anions into which it dissociates are both present in a state of true solution. But with a colloidal solution of an acid, e.g. silicic acid sols, the position is very much different. Silicic acid when freshly formed appears to be present in a state of true solution but rapidly polymerizes, giving rise to colloidal silicic acid. In parts II, III and IV (also Chatterjee [1939]) it has been shown that the sols give rise to hydrogen ion activities of the order of $10^{-4}N$. The free and total acids of the ultrafiltrates constitute a small fraction (about 10 per cent or even less) of those of the corresponding sols. Colloidal solutions of silicic acid, therefore, possess an intrinsic acid character, which is independent of the presence of foreign substances. The potentiometric titration curves of the sols with bases show

inflexion points in the acid region, between pH 's 4.3 and 5.4. Some typical titration curves are given in Fig. 3 reproduced from Chatterjee's [1938] paper.

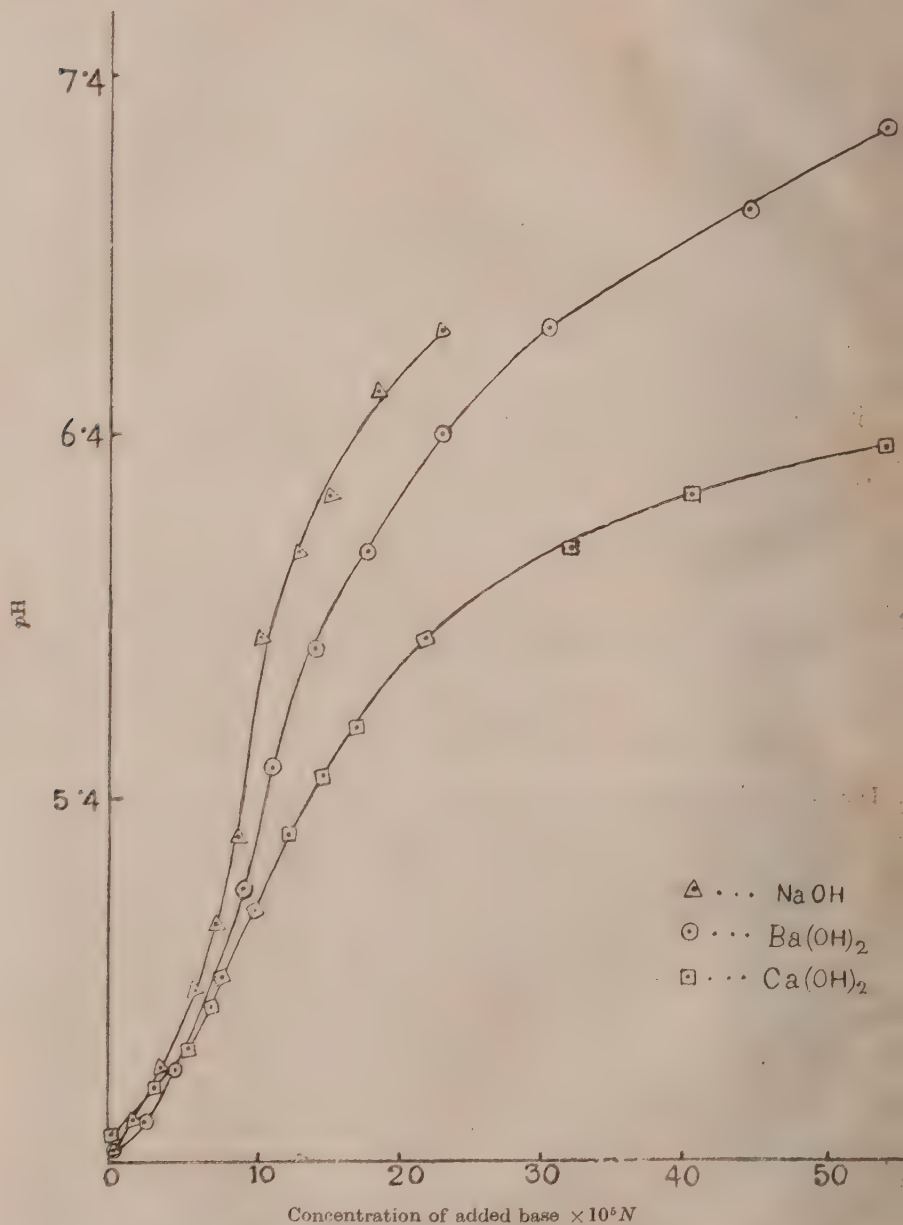


FIG. 3. Titration curves of silicic acid sol

The location of the inflexion point in the acid region is very significant in true solutions of acids would imply that the titrated solution contains a mixture of several acids of different dissociation constants and/or a basic acid. The negligible free and total acids of the ultrafiltrates indicate absence of any dissolved acid. Further, though not so significant, the titration curves do not show a second inflexion point till a pH of about 11.0 is reached. The inflexion point in the acid region is definitely characteristic of the colloidal solution of the acid. It signifies that there is a constant amount of hydrogen ions surrounding the colloidal particle at a definite level of affinity. A portion of these is free and is responsible for the observed e.m.f. of a hydrogen electrode and the remaining portion is 'bound'.

Different dilute bases give almost the same total acid when calculated from the first inflexion point in the corresponding curves. The amount of hydrogen neutralized at the inflexion point is thus a fixed quantity. The slopes of titration curves show that the intensities with which different bases react with the sol are in the order* $\text{Ca}(\text{OH})_2 > \text{Ba}(\text{OH})_2 > \text{NaOH}$. The greater acidity of $\text{Ca}(\text{OH})_2$ compared with $\text{Ba}(\text{OH})_2$ to react with the sol confirms the greater insolubility of calcium silicate compared with barium silicate observed by Joseph and Oakley [1925]. The degree of dissociation, if considered to be given by the ratio of the free acidity to the total acidity at the inflexion point, has values between 0.5 and 1.0.

The amounts of acid liberated by salts (added as chlorides) as shown by diminution in the pH are in the order $\text{Ba} > \text{Ca} > \text{Na}$.** On repeated leaching of silicic acid sols with a given concentration of a salt the amount of acid in the leachate gradually diminishes. The total amounts of acid obtained in the leachates are greater for BaCl_2 than for CaCl_2 at the same concentration of both. Moreover, both salts liberate much more acid than is obtained at the first inflexion point in the titration with the bases alone. It thus appears that 'bound' hydrogen ions are present in addition to those which react with the base at the first inflexion point. These hydrogen ions are therefore, held at the surface at a higher energy level. But the total quantity of the corresponding so-called salt that is formed by continued leaching is a small fraction of the number of moles of SiO_2 present. The reaction of the salt does not lead to the formation of a second solid phase and is limited to the surface. The maximum amount of acid which thus reacts with $N\text{-BaCl}_2$ has been found to constitute about 0.13 per cent of the total silicon dioxide.

The greater relative effect of Ba than Ca in the interaction with the salts in the acid region is definitely against the explanation that the development of acidity is due to the formation of insoluble silicates. It has already been mentioned that calcium silicate is more insoluble than barium silicate and consequently the order should be $\text{Ca} > \text{Ba}$, i.e. the reverse order of what has been observed. *Ad hoc* assumptions regarding changes of the relative order of solubilities of the barium and calcium salts in the acid region consequent on the formation of another type of salt or the existence of a different type of acid are therefore necessary from the usual chemical point of view to

* This order represents what has been called the irregular cation effect

** This order represents what has been called the regular cation effect as it agrees with the lyotrope series

explain these observations. The cation effects observed with silicic acid become more pronounced with hydrogen clays and soils. (Further discussion later).

Titration curves of silicic acid sols have been found to show a self-inflexion point at a higher pH value between pH's 11.0 and 11.8, dependent on the concentration of the sol. The total acid calculated from this inflexion point shows a fair agreement with the silica content (gm. mols. per litre) of the sol. The composition of the resulting salt at the inflexion point is $\text{Na}_2\text{O} \cdot 2\text{SiO}_2$. The buffer-capacity curves show only one maximum, near the point of half neutralization and it is justifiable to conclude that the salt formed is NaHSiO_3 . But the maximum value of the buffer capacity is considerably greater than that observed in the case of a dissolved acid having the same dissociation constant and total acidity. The greater buffer capacity arises from a continuous solution of the colloidal particles which act as a reservoir from which fresh quantities of the acid are supplied. Colloidal silicic acid behaves in its interaction at a high pH as a dibasic acid, its first dissociation constant is about 5.2×10^{-10} and its solubility of the order of 0.045 g/l. SiO_2 per litre at 30°C. Colloidal silicic acid thus constitutes a heterogeneous phase, of which a part, the charged colloidal particle, is definitely not in a state of true solution. The interaction is limited to the interface unless the pH is high enough to dissolve the particles and to hold the resulting silicic acid in true solution. The reaction is then no longer restricted to the interface and conforms to the usual type of chemical reaction between an insoluble acid and a base.

The electrochemical properties of hydrogen clay sols

Far greater complexities have been observed with hydrogen clays. These are discussed below. It will be shown that the theory of the double layer postulated by one of us [Mukherjee, 1921; 1922] provides a satisfactory explanation of their special features. The following simplified picture* of the double layer may be postulated for hydrogen clays. There is a primarily adsorbed layer of anions, presumably OH and O ions as indicated by X-ray [Kelley and Jenny, 1936] and other [Bar, 1935] investigations, built into the surface. An equivalent amount of hydrogen ions and, as will be shown later, aluminium ions, is held near the surface. A part of these H ions may be fixed by electrostatic forces or bound on the surface by chemical valence or Van der Waals type of forces. The remainder are osmotically active. They constitute the mobile sheet of the double layer and carry an electric charge equal and opposite to that of the free anions on the surface. The 'bound' ions are present in an osmotically inactive condition. The mobile hydrogen ions rise to the observed H-ion activity of the sol. On the addition of an electrolyte, an interchange takes place in the first instance between the cations of the electrolyte and the mobile H ions of the double layer. These cations can displace the bound H ions and are themselves adsorbed by simple electrostatic forces and/or by specific forces (chemical valence, or Van der Waals forces). What has been distinguished as electrical adsorption of ions carries

* It takes no account of the amphoteric character of hydrogen clay stressed by other workers [Mattson, 1932; 1937].

of the opposite sign to that of the primarily adsorbed ions is determined by electrostatic forces as given by their valency and diameter in the of hydration in which they occur on the surface, each of them forming an pair' with a primarily adsorbed ion on the surface. The state of hydration (or of dehydration) of the ion is of importance in relation to the energy of ion pair. In electrical adsorption the ion pair contains the oppositely charged ion (here, the cation) in the same state of hydration as in the solution. Lyotrope series of cations, $\text{Th} > \text{Al} > \text{Ba} > \text{Sr} > \text{Ca} > \text{Mg} > \text{Rb} > \text{K} > \text{Na} > \text{Li}$, flows from these considerations. When adsorption is brought about by physical or other specific forces, the energy of the resulting ion pair depends on chemical properties and the latter consequently determine the intensity of adsorption. Probably in the latter case the cation is adsorbed in a dehydrated condition. The various types of exchange observed by us between the ions of the double layer and cations of added electrolytes and their effects on the free and total acids of the sols and the form of their titration curves are discussed below.

Interchanges between H ions and cations of added salts

If only the mobile H ions are exchanged for the cations of the salt, no radical alteration in the H-ion activity of the sol will take place. That of the ultrafiltrate of the sol, on the other hand, will show a considerable increase indicating that H ions have been displaced from the double layer into the intercellular liquid. The following results illustrate this point.

TABLE III

of hydrogen clay sols and their ultrafiltrates in the presence and absence of salts of alkali metal cations

System	pH
I	4.52
ultrafiltrate of sol H	6.05
H + 0.0005N KCl	4.26
ultrafiltrate of above	4.42
H + 0.002N KCl	4.10
ultrafiltrate of above	4.15
Padegaon-B	4.54
ultrafiltrate of sol Padegaon-B	5.85
Padegaon-B + 0.0005N NaCl	3.85
ultrafiltrate of above	4.35

In the above experiments, the weak electrical adsorption of the K and Na ions and the low concentration of the salts are responsible for the

exchange being restricted to the mobile H ions alone. The variation in H-ion activity of the sols is consequently negligible.* Much larger variations indicating a displacement of the bound H ions are observed on adding concentrations of salts, specially salts of alkaline earth metals as the following results will show.

TABLE IV
Decrease of pH of hydrogen clay sols on the addition of different salts

Sol	Original pH	Salt added	Conc. of salt	Decrease in pH
E	4.66	NaCl	0.10N	1
		CaCl ₂	"	1
		BaCl ₂	"	1
H	4.52	NaCl	0.80N	1
		CaCl ₂	"	1
		BaCl ₂	"	1
I	4.51	CaCl ₂	0.25N	1
		BaCl ₂	"	1

The marked lowering of the pH of the sol on the addition of the salts indicates a displacement of mobile as well as bound H ions. Under similar experimental conditions practically no change in pH is observed with a solution of HCl having nearly the same pH as the sols. The relative effects of the different cations to liberate acid follow the order Ba > Ca > Na which is in agreement with the lyotrope series and the order of electrical adsorption of cations. The interaction of hydrogen clay with neutral salts, therefore, the cation effect is determined by electrostatic forces alone. It is a regular cation effect.

Similar to what has been observed with silicic acid sols, the reaction between the hydrogen clay and the neutral salts does not proceed to completion. The quantity of the so-called 'clay salt' formed as given by the amount of cation fixed by the hydrogen clay is less than the total quantity of acid liberated with the hydrogen clay as obtained on titrating it with a base, especially an alkaline earth hydroxide, in the presence of a salt.

The sol and salt mixture contains: (i) free H ions displaced into the micellar liquid from the double layer, and (ii) H ions, free and bound, associated with the flocs contained in the mixture†. When the mixture is titrated the free H ions are first neutralized and then as the pH rises more and more H ions are displaced from the flocs in presence of the salt to maintain equilibrium and neutralized. The large number of cations present in the mixture materially helps this process and the cation effect is emphatically shown by the fact that compared to the sol itself, the sol and salt mixture has a larger total acid or base exchange capacity (b. e. c.) measured at the initial pH.

* The slight lowering of the pH of the sol arises from a displacement of some H ions from the double layer.

† The part played by aluminium ions in determining the free and total acids of hydrogen clay and salt mixtures will be discussed later.

of the titration curve or at a fixed pH, e.g. 7.0. The higher the concentration of the salt in the mixture, the greater is the b. e. c. In the presence of a fixed concentration of different salts the b. e. c. decreases in the order $Ba > Na$ in agreement with the regular cation effect. The results given in Tables V and VI illustrate these points. The cation effect is really responsible for the observation often made that more base is required to attain a certain pH when the titration is carried out in the presence of a salt than in its absence. The H ions which are brought into a neutralizable condition on the addition of the salt to the hydrogen clay sol are not all displaced into the interlayer liquid. This is shown by the results given in Tables VI and VII. The smaller b. e. c. is obtained on titrating the clear supernatant liquid above the sediment of the sol and salt mixture and the extract obtained on repeatedly washing the sol with the solution of the salt than on titrating the mixture

TABLE V

exchange capacity in m. e. base per 100 gm. of oven-dried (105°C.) hydrogen clay using NaOH, Ba(OH)₂ and Ca(OH)₂

System	NaOH		Ba(OH) ₂		Ca(OH) ₂	
	At inflexion point	At pH 7.0	At inflexion point	At pH 7.0	At inflexion point	At pH 7.0
.. .. .	2.2(5.4)*	15.4	20.6(6.0)	25.0	21.5(5.8)	26.2
+ 0.1N NaCl	16.1(5.0)	26.4
0.1N BaCl ₂	28.0(4.6)	>42.2
0.1N CaCl ₂	21.2(4.4)	40.6
.. .. .	16.3(8.21)	6.30	17.5(7.10)	17.0	19.0(6.6)	19.5
+ 1.0N NaCl	22.3(7.0)	22.3
1.0N BaCl ₂	32.0 (5.4)	40.5
1.0N CaCl ₂	30.0(6.1)	32.5
.. .. .	18.8(7.5)	11.3	19.0(7.0)	19.0	20.5(6.4)	21.8
1.0N NaCl	21.25(6.0)	22.5
1.0N BaCl ₂	28.5 (5.5)	35.0
1.0N CaCl ₂	23.0(5.4)	26.5

The figures within brackets denote the pH at the inflexion point

TABLE VI

Base-exchange capacities calculated from the titration curves of the sol, sol + salt mixture and the clear supernatant liquid above the mixture, and the amounts of the cation of the salt adsorbed by the hydrogen clay before neutralization with the base

Conc. of BaCl ₂ added	B. e. c. at pH 7.0 in m. e. Ba(OH) ₂ per 100 gm. colloid obtained on titrating			M.e. Ba adsorbed per 100 g. colloid
	Sol H	Sol H + BaCl ₂ (in situ)	Supernatant liquid of sol H + BaCl ₂	
0	32.0
0.01N	..	33.0	11.4	11.1
0.02N	..	35.0	11.9	12.7
0.04N	..	37.5	14.4	15.2
0.09N	..	43.5	17.0	18.5
1.0N	..	48.0	22.0	24.2

TABLE VII

Base-exchange capacities obtained on titrating the sol + salt mixture, and successive portions of the salt extract

System titrated	B. e. c. at pH 7.0 in m. e. Ba(OH) ₂ per 100 gm. colloid
Sol H + 0.83N BaCl ₂	48.0
1st 100 c.c. of leachate	27.0
2nd " " "	3.0
3rd " " "	1.2

The last column of Table VI shows the amount of the cation (Ba) adsorbed by the hydrogen clay from the solution. This amount is, as is to be expected, in fair agreement with the b. e. c. calculated from the titratable acid in the supernatant liquid of the sol and salt mixture given in the fourth column of Table VI.

The above results show that routine methods in which neutral salt extracts of acid soils are titrated for estimating their exchangeable hydrogen and requirement give only a fraction of their total neutralizable acid or base. This is owing to an incomplete displacement of the H ions of the double layer by the cations of the salt. The back reaction set up by the H ions which have already been displaced in the intermicellar liquid is responsible for this incompleteness.

change. When, however, the sol and salt mixture is titrated *in situ*, these after H ions are continuously removed from the sphere of action and the neutralization is further helped by the large number of cations present in the medium.

Interchanges between H ions and cations of added bases

(1) *Variations of the b. e. c. obtained on titration with different bases.*—* Ion effects also play a definite rôle when the sols alone are titrated with bases. In titrating the sol, apart from the direct neutralization of the free ions by the OH ions of the base, its cations displace various amounts of bound H ions from the double layer which are then neutralized by the OH ions. The greater the displacement, the greater is the amount of acid reacting with the base at a fixed pH. Also, the higher the pH, the greater is the total acid or the base-exchange capacity (b. e. c.) with a given base. Titration with different bases gives different b. e. c.'s calculated both at the inflexion point of the titration curves as also at pH 7.0 as the results given in Tables V and VI will show.

TABLE VIII

Base-exchange capacity of hydrogen clay calculated from titration curves with different bases

Sol	Base used for titration	pH at inflexion	B. e. c. in m. e. base per 100 gm. colloid	
			At inflexion point	At pH 7.0
	NaOH	5.4	2.2	15.4
	Ba(OH) ₂	6.0	20.6	25.0
	Ca(OH) ₂	5.8	21.5	26.2
	Ba(OH) ₂	5.8	21.5	32.0
	Ca(OH) ₂	6.6	21.5	32.8
	NaOH	8.05	90.0	78.0
	Ba(OH) ₂	7.00	82.0	82.0
	Ca(OH) ₂	6.95	96.0	97.0
	NaOH	7.15	68.0	61.0
	Ba(OH) ₂	5.80	55.0	67.0
	Ca(OH) ₂	5.20	58.0	67.0

* Some results illustrating the variability of the b. e. c. of hydrogen clay have been discussed in part VI [Mitra, Mukherjee and Bagchi, 1940]

The b. e. c. of E, L and N calculated at the inflexion point as also at 7.0 decreases in the order $\text{Ca(OH)}_2 > \text{Ba(OH)}_2 > \text{NaOH}$. This is the order in which the b. e. c. at pH 7.0 of I and K varies. That of I calculated at the inflexion point follows the order; $\text{Ca(OH)}_2 > \text{NaOH} > \text{Ba(OH)}_2$. For K, the order is $\text{NaOH} > \text{Ca(OH)}_2 > \text{Ba(OH)}_2$. In comparing the b. e. c. with different bases the pH at which it is measured is an important factor. The inflexion points do not all occur at the same pH. The titration curves from which the b. e. c.'s have been obtained show that increasing amounts of the base react with the soil as the pH rises. The comparison should, therefore, be made at the same pH, e.g. pH 7.0. At this pH, the b. e. c. in all cases decreases in the order $\text{Ca(OH)}_2 > \text{Ba(OH)}_2 > \text{NaOH}$. The slopes of the titration curves also point to the same order of the capacity of the different bases to react with the hydrogen clays.

(2) *Features of titration curves.*—The cation effects also markedly influence the form of the titration curves. The study of these titration curves constitutes one of the important steps in the elucidation of the electrochemical character and the results previously obtained by us have been described in papers V, VI, VII and VIII. Bradfield [1927] was the first to obtain the titration curves of electro dialysed hydrogen clays and following him, the work has been continued by Bayer [1930], Bayer and Scarseth [1931], Denison [1933] and others. Bradfield observed that the curves 'were of the type to be expected for very weak acids' and showed an inflexion point at pH 8.5 for NaOH and 7.0 for Ba(OH)_2 . He found that both the bases gave the same b. e. c. at their respective inflexion points. Bayer [1930] found a constant b. e. c. with the strong bases. But it will be seen from his paper that the pH at inflexion decreases in the order $\text{LiOH} > \text{NaOH} > \text{KOH} > \text{Ba(OH)}_2 > \text{Ca(OH)}_2 > \text{Mg(OH)}_2$. According to Bradfield and Bayer this was the order in which the corresponding salts of the clay acid were hydrolysed in an aqueous medium, but one might ask for the reason of the difference in the behaviour of these strong bases. The conductometric titration curves of Bradfield and Bayer also resembled that of a weak monobasic acid. Bradfield, on the whole, considered that the reaction between a hydrogen clay and a strong base is an ordinary neutralization process and that 'recourse to the adsorption theory seems unnecessary'. However, some of his own observations are certainly difficult to explain in the light of the simple picture suggested by him. Thus, while the end point of his conductometric titration curve with caustic soda gave the same total acid as the inflexion point of the potentiometric titration curves with this base and barium hydroxide, the end point of the conductometric curve with baryta gave a much larger total acid and this curve had also a somewhat different shape compared with the conductometric curve with caustic soda. Its initial portion was flatter and the end point more rounded. To explain these differences, Bradfield postulated the formation of insoluble products by the interaction of hydrogen clay with alkaline earth hydroxides. It is, however, difficult to see how the formation of such insoluble products would affect the forms of the potentiometric curves in the manner described by him. A simple parallel case is illustrated by the formation of calcium citrate from citric acid and calcium hydroxide. On the gradual addition of the base to the acid more and more calcium citrate will precipitate and the pH will very slowly rise till all the acid has been neutralized. Further addition of the base will result in a sharp rise of the pH.

be observed if the base were added to water. The titration curves of acid sols with baryta or lime (Fig. 2) illustrate the case where the weak acid and the resulting salt are both almost insoluble. The features characteristic of the above two cases are not shown by the titration curves of hydrogen clay sols obtained by previous workers and by us (discussed below). For example, the inflexion point is not as sharp as might be expected and the curves indicate a pronounced buffer-action beyond the inflexion point. According to Field [1927] 'this latter feature is difficult to explain'. The following observations made by us further illustrate the difficulties in the way of accepting the true weak monobasic acid character of hydrogen clay sols as postulated by Field and others.

In contrast to the sharp initial rise of the potentiometric titration curve with NaOH (Fig. 4) which indicates a weak acid character, the conductometric titration curve with this base shows a comparatively sharp minimum, characteristic of the titration of a strong or a moderately strong acid by a strong base. Such a minimum would not be observed if the sodium salt of the acid underwent a marked hydrolysis. On the other hand, the conductivity would increase from the beginning of the titration as actually observed by both Field and Bayer. In our work with about 40 hydrogen clays and suspensions of hydrogen clay having silica/alumina ratios ranging from 1.87 to 10.0 and prepared from soils of widely different origin, a sharp minimum has been observed without exception in the conductometric titration curve with HCl. It is possible that Bradfield and Bayer missed this minimum owing to the large quantities of the alkali being added from the beginning of the titration. We have observed that the minimum in the conductometric titration curve with NaOH gives only a small fraction of the base-exchange capacity, usually 10-20 per cent, calculated from the inflexion point of the corresponding potentiometric titration curve, which lies between pH 7.0 and 8.0. Beyond the minimum the conductometric titration curve shows a break and the b. e. c. calculated from this break agrees with that obtained from the inflexion point of the potentiometric titration curve. The conductivity minimum is real and cannot be referred to the neutralization of any dissolved acid or acids present as impurity in the sol as the titration curve of the ultrafiltrate of the sol shows no such minimum. In fact, the ultrafiltrate contains no titratable acid (Table II). Its pH ranges from 5.8 to 6.8 according to the degree of purification of the sol, while that of the sol lies between 4.0 and 4.8 in agreement with the 'suspension effect' of Wiegner and Mann [1929]. The pH of the sol depends on the amount of the solid material contained in a given volume of the sol.

A second objection against the 'weak acid' theory is the fact that the dissociation constant K calculated from different points of the NaOH curve (which shows the greatest resemblance with that of a weak acid) with the aid of the well-known Henderson equation has been found to have different values (e.g., 1940). The concentration of the salt was taken as equal to that of the base added and the concentration of the unneutralized undissociated

The potentiometric titration curve with NaOH of some hydrogen clays, e.g. that shown in Fig. 5 shows an inflexion point in the acid region in addition to the one in the alkaline region (discussed later). In such cases, the minimum of the conductometric titration gives nearly the same total acid as the inflexion point in the acid region.

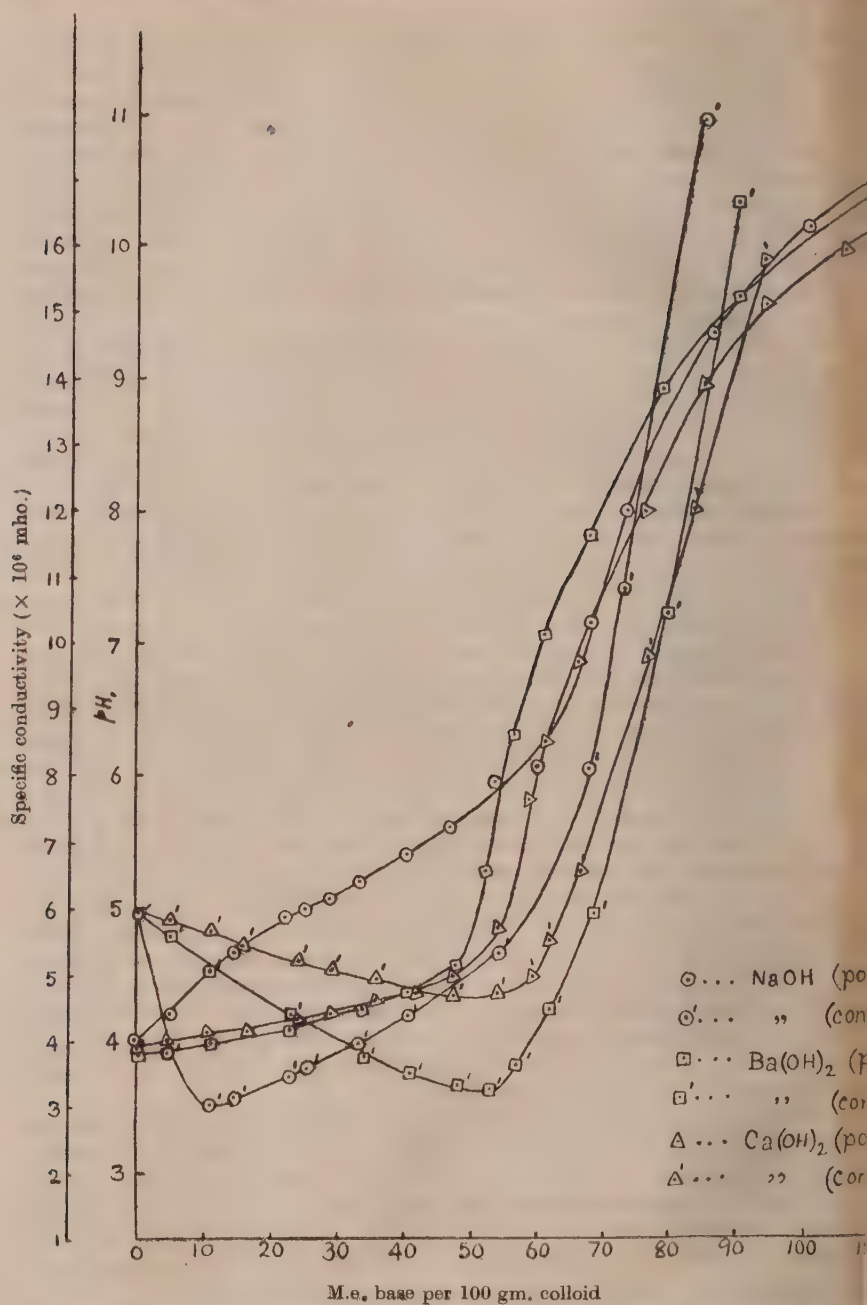


FIG. 4. Potentiometric and conductometric titration curves with NaOH, $\text{Ba}(\text{OH})_2$ and $\text{Ca}(\text{OH})_2$.

acid as equal to $C-B$ where C is the total acid * given by the inflexion point on the titration curve. Further, the dissociation constant calculated in the above manner does not agree with that given by the other mass action equation

$$K = \frac{\alpha^2 C}{1-\alpha} \text{ where } \alpha \text{ is the ratio of the free acid of the sol to the total acid } C$$

and may therefore be called the degree of dissociation of the sol. α has a very small value even at total acid concentration of the order of $10^{-4} N$ which is in agreement with the weak acid character of the NaOH curve (potentiometric). But a strong acid character of the sol is indicated by its potentiometric titration curves with $\text{Ba}(\text{OH})_2$ and $\text{Ca}(\text{OH})_2$.

Some of our potentiometric titration curves with NaOH show a dibasic acid character. Those of hydrogen clays F and Latekujan-F and hydrogen bentonite Hati-Ki-Dhani-B show this feature. (Fig. 5)**

The first inflexion occurs near about pH 5.0 and the second between 7.0 and 8.0. The initial portion of the titration curve of F has the appearance of that of a strong acid, and the weak acid character of the NaOH curve (potentiometric) of K shown in Fig. 4 is absent. These individual differences in the form of the titration curves are likely to be useful in the characterization and classification of soils [Anderson and Byers, 1936]. They have been more fully dealt with in part VIII [Mukherjee, *et al.*, 1942]. They further show that in error might easily be made in drawing any general conclusion regarding the acid character of hydrogen clay unless supported by observations on a sufficiently large number of hydrogen clays prepared from soils of widely different origin and type.

Of about 50 hydrogen clays and their sub-fractions studied by us the potentiometric titration curves with alkaline earth hydroxides of only one hydrogen clay, N, and two sub-fractions of L and the hydrogen bentonite Shadres-B showed a weak acid character. The titration curves with these bases of all other hydrogen clays have a slowly rising initial portion which shows a more or less marked inflexion point as would be observed in the case of a strong or moderately strong acid. The corresponding conductometric titration curves, however, show a weak acid character (Figs. 4 and 6). These mutually conflicting features of the two sets of titration curves are not possible to reconcile if the interaction between the hydrogen clay and the base is considered to be a simple neutralization process.

The $\text{Ba}(\text{OH})_2$ and $\text{Ca}(\text{OH})_2$ curves of the majority of the hydrogen clays give an inflexion point between pH's 5.5 and 6.3; for a minority the inflexion point lies between pH's 6.3 and 7.0, and in a few cases the inflexion point has been found in the weakly alkaline region although the initial portion of the titration curve shows a strong acid character. The occurrence of the inflexion point near about pH 7.0 observed with some hydrogen clays is consistent with the strong monobasic acid character of the titration curves. Its occurrence in the acid region which is more common indicates, according to usual concepts of electrochemistry as pointed out in the case of silicic acid sols, that the hydrogen clay is either a mixture of several dissolved acids having different

*This total acid given by the inflexion point does not represent all the neutralizable acid present in the system

**Sub-fractions of Hati-ki-Dhani-B and Latekujan-F also have a dibasic acid character

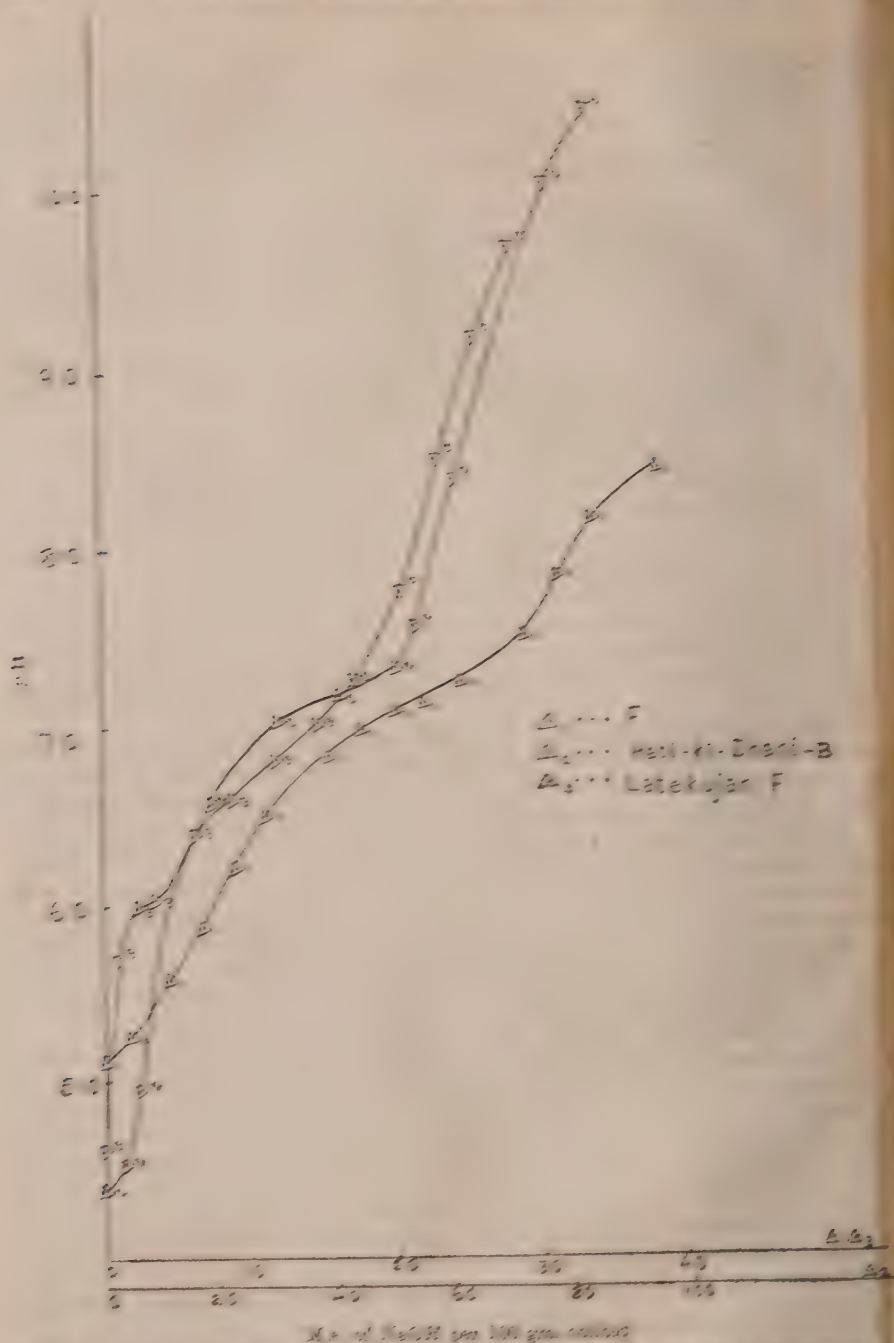


FIG. 5. Pseudomonas cellulosa curve with NaOH of 4.0 mmole hydrogen chloride and hydrogen bromide.

dissociation constants or it is a polybasic acid. The fact that the ultradilution of the sol contains negligible free and total acids rules out the first possibility. The sol cannot also be considered to be an ordinary polybasic acid whose various dissociation constants have markedly different values as the titration curve shows no second inflexion even when the titration is extended to pH 12.5*. Above this pH, the hydrogen clay is likely to decompose.

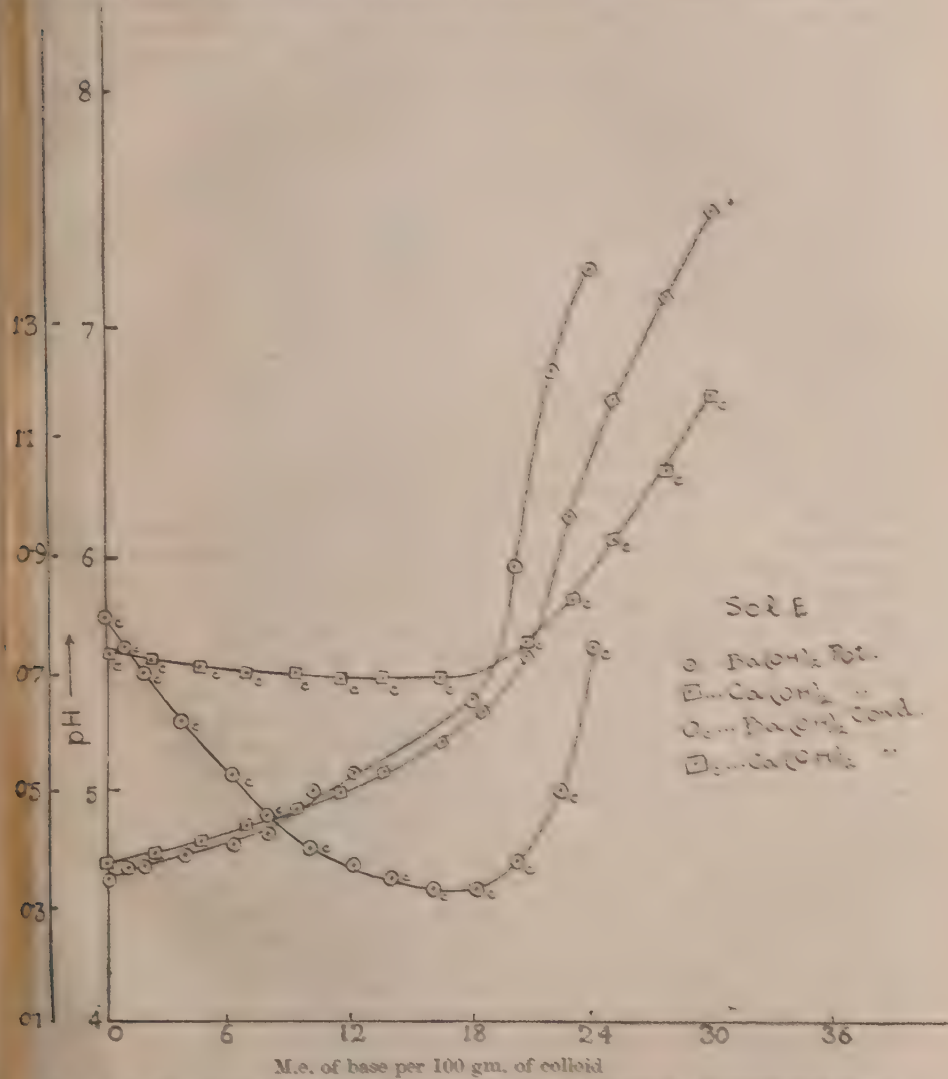


FIG. 6. Potentiometric and conductometric titration curves of hydrogen clay with $(OH)_2$ and $Ca(OH)_2$.

* Of course, if the dissociation constants do not differ much from one another, other inflexions will not be observed.

The picture postulating the existence of mobile and bound H ions on the surface and their exchange for the cations of an added base or salt provides a consistent explanation of the slopes of the titration curves including the apparently contradictory features of the potentiometric and conductometric curves discussed above. The first additions of the base neutralize the mobile H ions. This displaces the equilibrium between mobile and bound H ions which is restored by the passage of some bound H ions from the bound to the mobile condition. Adsorption of the cations of the base facilitates this process. When barium or calcium hydroxide is the base used, the Ba or Ca ions, because of their strong electrical adsorption, displace more and more bound H ions from the beginning of the titration and the H ions thus displaced are neutralized by the OH ions of the base. The titration curve (potentiometric) has, therefore, a flat run (Figs. 4 and 6) indicating a moderately strong acid character. When the limit to which the bound H ions can be displaced (by the cation of the base used) and neutralized has been reached further addition of the base results in a sharp rise of the pH, that is the titration curve shows an inflexion point. This limit, however, does not correspond to the neutralization of all the bound H ions. And the titration curve shows a continued buffer action beyond the inflexion point. Also, as previously shown, titration in the presence of a large concentration of a neutral salt yields a much larger b. e. c. The inflexion point in the titration curves with base thus indicates the neutralization of H ions up to a definite affinity level.

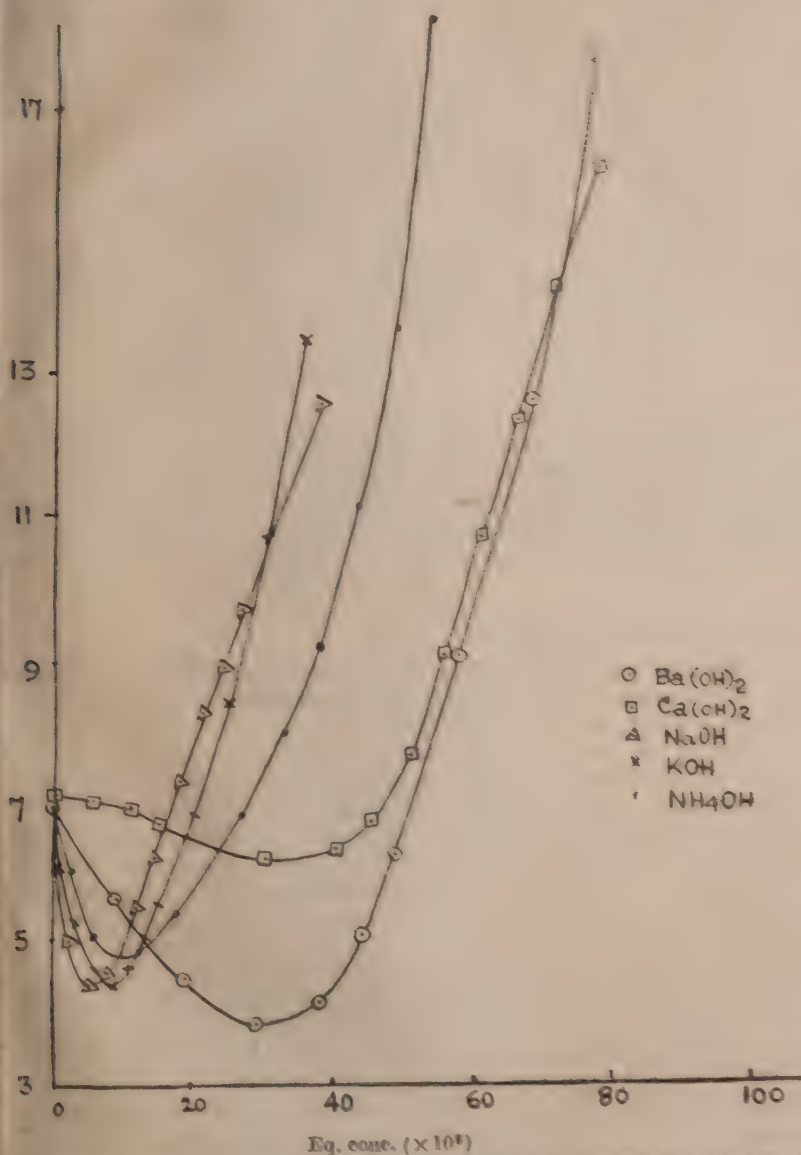
Using sodium hydroxide also, the first additions of the base would similarly neutralize the mobile H ions. The bound H ions which far outnumber the mobile H ions* cannot be easily displaced from the double layer by the Na ions because of their weak electrical adsorption. The pH of the system therefore, shoots up and the titration curve shows a comparatively sharp initial rise. On further addition of the base, the concentration of Na ions in the system increases and with it, their adsorption on the surface. This combined with the gradually increasing pH of the system, helps in the neutralization of more and more bound H ions and the titration curve shows flattening after the initial rise. When the limit to which the bound H ions can be so displaced and neutralized has been reached, further addition of base results in a sharp rise of the pH, that is, the titration curve shows an inflexion. Fig. 4 (also Figs. 8 and 9) illustrates these features.

The electrical adsorption of the cations of the base also influences the slopes of the conductometric curves and the considerations set forth above account for their features. The greater the adsorption the more bound ions will be displaced and neutralized at a given pH and the slope of the curve will resemble that of a weak acid. The $\text{Ba}(\text{OH})_2$ and $\text{Ca}(\text{OH})_2$ curves (conductometric) given in Figs. 4, 6 and 7 show these features.

The displacement of bound H ions and their neutralization would also diminish the slope of the potentiometric titration curve but in this case smaller slope indicates a stronger acid. The NaOH curve (conductometric) has the greatest downward slope though the corresponding potentiometric curve shows the steepest initial rise, thus indicating the weakest acid character.

*This is shown by our observation that hydrogen clay sols have a small ratio (less than 10 per cent) of the free acid to the total acid calculated from the inflexion point in the titration curve with a dilute base.

slopes (of the descending portions) of the conductometric curves are arranged in the order: $\text{NaOH} > \text{KOH} > \text{NH}_4\text{OH} > \text{Ba}(\text{OH})_2 > \text{Ca}(\text{OH})_2$ (Fig. 7). The slopes observed with sol F have been compared with the theoretical* slopes in Table IX.



7. Conductometric titration curves of hydrogen clay with NaOH , KOH , NH_4OH , $\text{Ba}(\text{OH})_2$ and $\text{Ca}(\text{OH})_2$.

* The theoretical slope is given by $(U_{\text{H}^+} - U_{\text{M}^+})/1000$ where U_{H^+} and U_{M^+} respectively the mobilities of H^+ ion and M^+ the cation of the base.

TABLE IX

Observed and calculated slopes of condensation reaction curves of hydroxy-
city with various bases

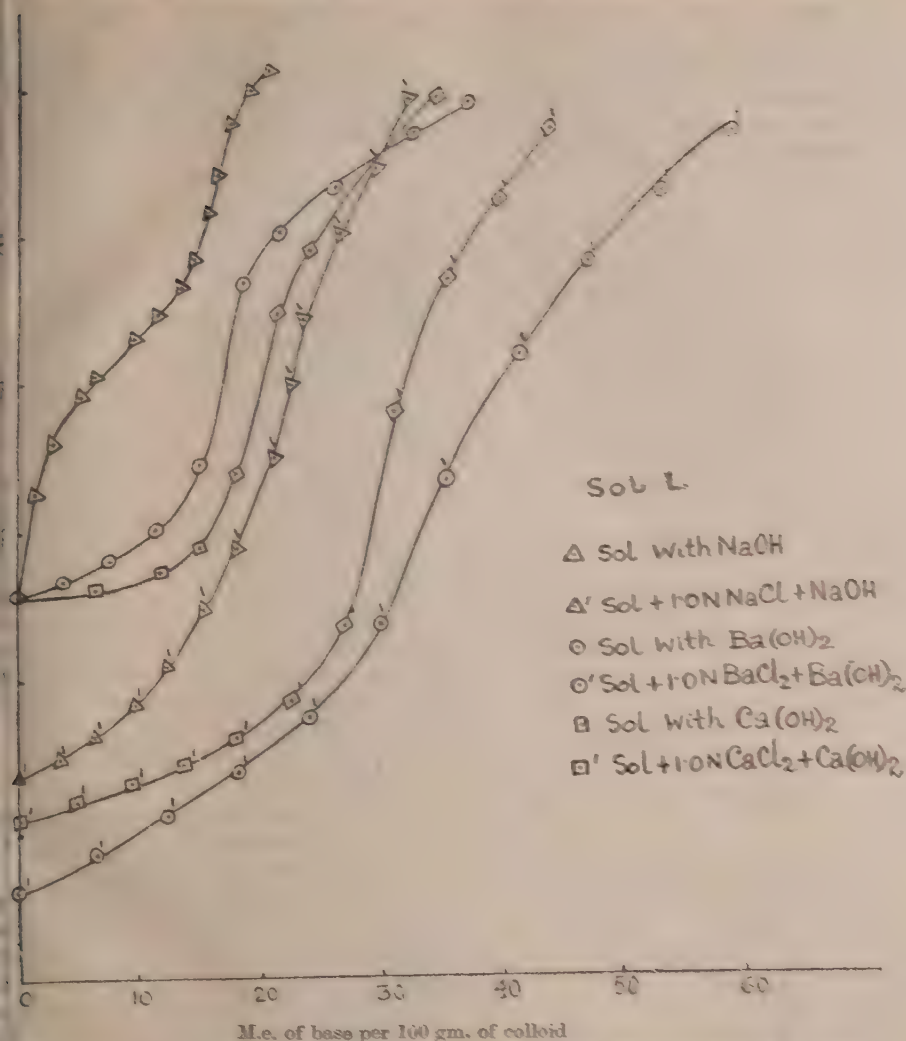
Base used	Slope of condensation curves	
	Observed	Calculated
NaOH	0.340	0.3
KOH	0.365	0.3
NH_4OH	0.335	0.3
$\text{Ba}(\text{OH})_2$	0.375	0.3
$\text{Ca}(\text{OH})_2$	0.365	0.3

The observed slope is always less than the theoretical one. The great discrepancy is noticed with the $\text{Ba}(\text{OH})_2$ and $\text{Ca}(\text{OH})_2$ curves, which is due to the strong electrical adsorption of the cations of these bases. The true slopes of these two curves confirm the conclusion previously made in the interaction with the bases alone. It is now left to consider effect the ions.

Regular and specific cation effects

The main features of the cation effects described in the previous section and their importance in various methods of estimation of the $\text{S} + \text{C} + \text{O}$ of and between bases are discussed below.

The effect of cations in determining the lime requirement and base-his content of soil has been recognized by several workers (Frostner and McIlroy, 1935; Hardy and Lewis, 1937; Clark and Gilman, 1938; Harrison, 1939). The exact nature of the cation effect, however, has not been clearly defined. The results show that this cation effect varies in certain respects with the acid and the treatment made in the previous section between the regular and the specific effects taken account of this variation. The regular cation effect observed in the interaction with the same soil with bases in the present study character is the acid region. The soil and soil mixture contains a relatively amount of free acid, its pH being often as low as 3.5 depending the nature and concentration of the soil added, while that of the soil itself was about pH 4.5. The interaction with bases in the presence of cations usually takes place in the acid region usually between pH's 3.5 and 4.5 and consequently here the regular cation effect is observed. The titration curve of free acid and soil mixture starts from a pH near about 3.5, has a sharp rise to the inflection point of the acid with the same base and usually has an inflection point between pH's 4.5 and 5.5 (Table V and Figs. 5 and



Potentiometric titration curves of hydrogen clay L in the presence and absence of salts

The specific cation effect observed in the interactions with the bases, on the other hand, operates in the weakly acid to alkaline region. The titration curves with the bases, especially those with NaOH, are less buffered in this region compared with the titration curves of the sol and salt mixtures and the inflection point occurs at a much higher pH, usually between 5.5 and 6.5 (Table VI).

Reference has been previously made to the lack of agreement between the values of the base-exchange capacity (b. e. c.) of soil obtained by various routine methods. Using a number of hydrogen clays, comparison of different routine

methods shows [Mitra and Mitra, 1940; Mukherjee *et al.*, 1942] that disagreement arises from the fact that sometimes the pH and, more generally, the cation effects which operate in the several methods are not the same in quantitative sense. Concordant results have, however, been obtained: the same type of cation effect is involved at the same pH and equilibrium conditions are considered.

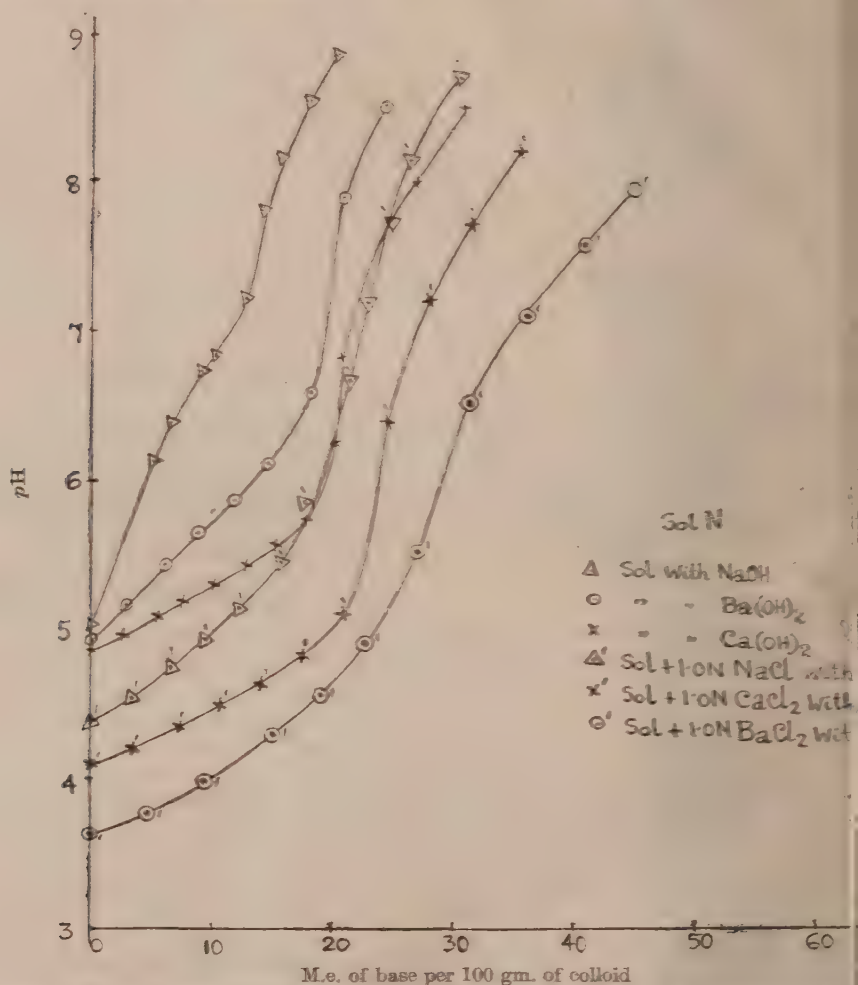


FIG. 9. Potentiometric titration curves of hydrogen clay N in the presence and absence of salts

A simple explanation of the cation effect and especially of its variation with the pH is not easy to offer in the light of the classical concepts of colloid chemistry. The product of the interaction between hydrogen clay and monovalent and bivalent cations has often been regarded as an ordinary salt, the so-

'clay salt' and considerations of solubilities and degrees of dissociation of such clay salt have often been brought forward to explain the nature of such interactions and equilibrium conditions. Mattson [1932; 1935; 1937] has considerably developed this view. He postulates that, unlike ordinary salts, the clay salts are dissociated only to a limited extent and in the interaction $H.AB.OH + MA' \text{ (or MOH)} \rightleftharpoons M.AB.OH + HA' \text{ (or HOH)}$ between the hydrogen clay $H.AB.OH$ and the salt MA' or base MOH , the smaller the degree of dissociation of the clay salt $M.AB.OH$, the greater will be the displacement of the equilibrium to the right hand side of the equation. He postulates further that the salt (MA') suppresses the dissociation of the compound ($M.AB.OH$) which the salt forms with the complex resulting in a further displacement of the equilibrium to the right hand side of the equation; the effect is similar to the suppression of the solubility of a salt by the addition of another having an ion in common. According to him, in the titration of the sol and salt mixture, therefore, 'a lot of anions is not produced to suppress the dissociation of the acid' and consequently, compared with the sol itself the titration curve of the mixture gives a larger total acid at a fixed pH.

It has been previously shown that if the heterogeneous nature of the system is not taken into consideration, the concepts of the degree of dissociation and dissociation constant have little significance in the case of even such simple polyphase acid systems as saturated solutions of acids containing excess of the solid phase. The difficulties are more pronounced and differ even in character with colloidal solutions of acids, e.g. hydrogen clays. Further, solubility considerations have no real meaning with the so-called clay salt in the absence of any definite evidence to show that it forms a separate solid phase or an isomorphous mixture. The interaction has been shown to be limited to the surface. Finally, such considerations cannot reconcile the differences in the relative effects of cations, e.g. the Ba and Ca ions, in acid and alkaline regions as observed by us unless further *ad hoc* assumptions regarding changes in the relative solubilities of the barium and calcium 'clayates' with the pH are made to fit the observations.

A consistent explanation of the cation effects and of the interactions of hydrogen clays in general has been previously given on the basis of the concepts of primary and secondary adsorption of which latter electrical adsorption forms a particular type as postulated by one of us [Mukherjee, 1921; 1922]. The primarily adsorbed anion is fixed on the surface, while the adsorbed cation is present on the liquid side of the double layer. The two form an 'ion pair' which is fundamentally different from an ordinary salt molecule formed by the interaction between an acid and a base present either in the dissolved condition or in the solid state. The salt molecule has a definite solubility and it either remains in solution or separates out as a solid phase. The ion pair, however, is present in a peculiar phasal condition being present only on the surface. Besides a proportion of the cations neutralising the negative charge is present in the liquid and is thus in a dissolved condition, while the other part of the salt, the anion, is fixed on the solid surface and should thus be considered insoluble. Consequently, the ion pair as a whole can have no definite solubility in the usual sense.

The above picture has much in common with that suggested by Wiegner [1925; 1931]. The main difference consists in postulating the forces by which

the cations are held near the surface and, specially, the variation in the nature of these forces with the pH . Wiegner and Jenny [1927] also suggested the existence of electrical and specific forces of attraction to account for their observation that the alkaline earth metal cations are often adsorbed and released in different orders. They considered that adsorption was always brought about by electrical attraction. Once the cations were taken sufficiently near the surface by electrostatic attraction, they combined with the anion residues on the surface by more specific forces, e.g. chemical affinity, and the subsequent release of the cations from the resulting combinations depended on the nature and intensity of the binding force. Our work shows that adsorption itself may take place through electrostatic attraction as also more specific forces and, what is more important, the pH determines the nature of the force that operates.

The variations of free and total acids previously discussed point to the presence of H^+ ions in different levels of reactivity (or affinity) on the surface. Of these, (1) the free, i.e. the osmotically active H^+ ions present in the mobile sheets of the double layer are the most reactive and they give rise to the free acidity, that is the observed e.m.f. of the hydrogen or glass electrode. They are easily neutralized by OH^- ions and displaced by osmotic interchange with the cations of an added salt even if the latter are alkali metal cations and are present in small concentrations. In addition to these mobile H^+ ions, there are (2) H^+ ions secondarily adsorbed or bound which react with OH^- ions of the added base independent of the nature of its cations. In other words, in addition to the free H^+ ions there are bound H^+ ions on the surface which come out when the pH of the soil is increased. Lastly there are (3) H^+ ions at a much higher affinity level which are released by strongly adsorbed cations whose nature and concentration determine the number of bound H^+ ions set free at a comparatively low pH . The inflexion point in the titration curves with bases alone indicates in addition to the neutralization of H^+ ions of the second category that of some H^+ ions of the third category. A large number of these latter H^+ ions are neutralized (at the inflexion point) when the soil is titrated in the presence of a large concentration of a neutral salt. A high concentration of a strongly adsorbed cation together with a high pH makes reactive the largest number of bound H^+ ions. The limit to which the pH can be raised is conditioned by the stability of the adsorption complex. By making a suitable choice of the salt and its concentration it may be possible to reach a limiting value of the total acid, that is the b.e.c. Unpublished results of S. K. Mukherjee of this laboratory indicate the existence of such a limiting value. The b. e. c. given by Schofield's [1933] method approaches this limit.

The acid character of hydrogen clay in relation to some problems of soil science

An outline of the fundamental electrochemical character of hydrogen clay as an acid system has been given above. The manner in which it varies with some other properties of the hydrogen clay is indicated below. Details of these investigations will be published in separate series of papers.

Variations in the properties of sub-fractions of hydrogen clay

Sub-fractions of a hydrogen clay obtained by the graded centrifugalization of the entire clay fraction have been found to show the same broad feature

g. the regular and specific cation effects, as the entire hydrogen clay fraction. The base-exchange capacity (b.e.c.) of the different fractions usually increases with diminishing particle size as observed by other workers [Marshall, 1935]. However, the b.e.c. calculated per sq. cm. of the external surface* does not usually remain constant, showing that the reaction with the base is not confined to the outer surface. The difference may also arise from the observed differences in the mass chemical compositions of the different fractions. The variations in chemical composition may arise from: (a) varying admixtures of free silica and sesquioxides in the different fractions, (b) the presence of different clay minerals in the various fractions, and (c) isomorphous replacements within the lattice of the same mineral contained in the different fractions. (b) and (c) would probably give rise to some definite alterations in the forms of the titration curves of the different fractions. Actually, however, the titration curves usually have more or less the same form, showing that the various fractions have fundamentally the same mineral constituent. An interesting observation made with most of the sub-fractions is the fact that their b.e.c. usually increases with a decrease in the silica-sesquioxide ratio. A positive correlation between the b.e.c. and this ratio is, on the other hand, usually observed with entire clay fractions [Mattson, 1932].

Our subsequent work on the sub-fractions includes, in addition to the above electrochemical studies, investigations on their X-ray and optical properties and their mineralogical compositions.

Alterations in the properties on the removal of 'free' silica and sesquioxides

The hydrogen clays have been found to show the same general features, e.g. the cation effects, both before and after removal of the free inorganic oxide contained in them. These features are thus characteristic of the exchange complex itself. Definite variations in the b.e.c. were often observed on the removal of the free oxides. Using Mattson's [1932] method for this purpose a decrease in the b.e.c. was always noted. Tamm's [1922] method gave rise to a decrease in the case of some hydrogen clays, while with others, an increase was observed. In no case, a decrease in the b.e.c. was observed using Drosdoff and Truog's [1935] method. The b.e.c. either increased or remained unaltered. An increase in the b.e.c. has always been observed using the method of Truog *et al.* [1936].

The rôle of aluminium ions in the interactions of hydrogen clays

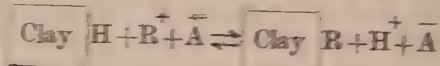
The rôle of aluminium ions in the interactions of hydrogen clays and acid soils with neutral salts is a much discussed problem. Some workers [Page, 1926; Wilson, 1929] consider that the acid liberated by the salt dissolves Al ions from the adsorption complex, while others [Daikuhara, 1914; Kappen, 1916] hold that a direct exchange of Al ions for the cations of the added salt takes place. The following are the possible sources of the displaced Al ions: (a) free Al_2O_3 contained in the hydrogen clay which is dissolved by the acid liberated; (b) Al ions forming the lattice of the mineral constituents of the clay; and (c) Al ions present on the surface in a secondarily

*In calculating the external surface, a spherical symmetry of the particles and a constant density of the different fractions were assumed.

adsorbed condition. Aluminium in all these three forms may react with acids, bases and salts. Toxic properties of acid soils are often attributed to the aluminium found in the soil solution [Comber, 1934]. It has been found [Mukherjee *et al.*, 1931; also unpublished work of Majumdar], however, that Al ions are stable on the surface of colloidal particles of aluminium oxide sols at a pH as high as 4.0. Fuller information regarding the part played by Al ions in the interactions of hydrogen clays under different conditions is therefore desirable.

It has been observed [Mukherjee and Charterjee, 1942] that the titratable acidity of the neutral salt extracts of hydrogen clay is sometimes greater than can be accounted for by the amount of aluminium present in the extract when low concentrations (e.g. up to 0.002N) of the salt are used. The amount of aluminium increases with the concentration of the salt and at a sufficiently high concentration (usually near about 1.0N, using salts of the alkaline earth metal cations) it has been found to be almost equal to the titratable acidity. At very low concentrations, e.g. up to 0.002N using salts of the alkali metal cations, only hydrogen ions are displaced.

The hydrogen-ion activity increases on the addition of the salt and favours the back reaction in the simple schematic equation given below :



As the concentration of the salt increases, more and more Al ions are exchanged at the expense of H ions, but the two processes do not seem to be independent of each other although, as already stated, only H ions are exchanged at the lower concentrations of the salt. Experiments in which the pH was kept constant by the use of suitable buffers showed that the amount of aluminium liberated is the same as that when no buffer were used and the pH allowed to decrease as a result of the addition of the salt. The relation between the amount of Al liberated at a constant pH and the concentration of the added salt is given by a curve which closely resembles the adsorption isotherm. All these results indicate the presence of Al as well as H ions on the surface of the hydrogen clay particles. Ions of both categories are directly exchanged for the cations of the added salts.

SUMMARY

The hydrogen clay is the inorganic part of the soil adsorption complex whose exchangeable cations have been replaced by H ions. It is usually made up of one or more secondary clay minerals, some comminuted primary minerals and 'free' oxides of Si, Al and Fe. The ensemble is an essentially electrochemical system—an electrolytic colloid with a dominant acid character. The main object of this investigation is the elucidation of this acid character.

Hydrosols of hydrogen clays are definitely polyphase acid systems, the insoluble acid material consisting of one or more phases and the intermicellar liquid another. While the sol has free acid usually of the order of 10^{-4} N, its ultratitrate shows an almost neutral reaction.

The interpretation of the titration curves constitutes an important step in the elucidation of the acid character. With this idea, hydrogen clay has

n titrated under various conditions and the features of the titration curves have been carefully analysed. The titration curves of the following simple two-phase acid systems which are amenable to more straightforward theoretical treatment than the complex hydrogen clay have also been studied: (i) titrated solution of cinnamic acid containing the solid acid; (ii) palmitic acid stearic acid hydrosols; and (iii) hydrosols of silicic acid.

The titration curves of cinnamic acid in the presence of the solid phase illustrate the difficulties in interpreting titration curves of heterogeneous acid systems. Kinetics of surface reactions play a definite rôle. The total amount of the acid taking part in the reaction is not constant but depends on the amounts of the alkali added. The course of the titration curve, however, can be fully understood knowing the solubility of the acid, its dissociation constant in true solution and the solubility of the resulting salt, sodium cinnamate. For the complex hydrogen clay the necessary information is lacking.

The titration curves of stearic acid sols with alkaline earth hydroxides illustrate features which would be expected if the hydrogen clay hydrosol were a heterogeneous acid which gives an insoluble salt like Ba- or Ca-stearate. Apart from some minor discrepancies the course of the titration curves of the stearic acid sol is fully accounted for by the phase rule.

Complexities are observed with silicic acid sols. The hydrogen ion activities, total acidities and the titration curves of the sols with bases differ in several essential respects from those of truly dissolved acids or from colloidal solutions of stearic acid. The total acidities at the first inflexion point are the same when titrated with sodium hydroxide as with barium or calcium hydroxide, but the slopes of the curves show a stronger adsorption of the alkaline earth metal ions. The first inflexion point occurs in the acid region between pH 4.3 and 4.7 and would indicate, for acids in true solution, that a polybasic acid and/or a mixture of acids of different strengths are present in the solution. Analysis of the ultrafiltrate shows that dissolved acids cannot be held responsible for the course of the titration curve including the inflexion point in the acid region. The interaction with the alkali continues beyond this inflexion point. Further, when a barium or a calcium salt is added to the system an amount of neutralizable acid considerably larger than the total acidity at the first inflexion point is liberated. This inflexion point, therefore, in no sense corresponds to the neutralization of all the hydrogen ions capable of reaction and the degrees of dissociation or dissociation constants calculated on the assumption that the amount of acid neutralized at the inflexion point represents the total neutralizable acid present in the system, lose their usual significance. The hydrogen ions liberated by neutral salts pass into the ultrafiltrate but additional hydrogen ions are still present in the system. This is shown by the results of continued leaching. A definite secondary effect associated with the energy of the formation of an ion pair by secondary adsorption is indicated. The complete titration curve of the sol with sodium carbonate shows on first examination that the sol appears to be a mixture of a moderately strong acid and a weak acid in true solution and that the latter is present in a very much greater concentration than the former. Calculations of the slopes of the conductometric and potentiometric curves and of the buffer indices show, however, that the resemblance is superficial.

Hydrogen clay sols present striking differences from acids in true solution. The total reacting acid or the base-exchange capacity (b.e.c.) of hydrogen clay is not a fixed quantity but depends on pH and cation effects. Usually the greater the pH the greater is the b.e.c. The cation effect is illustrated by (a) the dependence on the cation of the base of the b.e.c. calculated at the inflexion point and more strikingly at a fixed pH, e.g. 7.0; (b) by the much higher b.e.c. obtained on titration in the presence of a large concentration of a neutral salt than in its absence; and (c) by the different effects of various neutral salts having a common anion. In the absence of salts the b.e.c. decreases in the order $\text{Ca(OH)}_2 > \text{Ba(OH)}_2 > \text{NaOH}$ which, however, changes to $\text{Ba(OH)}_2 > \text{Ca(OH)}_2 > \text{NaOH}$ in the presence of a fixed concentration of the corresponding salts. The reversal in the relative effects of Ba and Ca has been traced to the differences in the pH region in which the acid-base reaction takes place. In the presence of the salt the interaction with a greater portion of the base Ba(OH)_2 or Ca(OH)_2 up to the inflexion point occurs in the acid region, usually between pH 3.5 and 5.5; while in the absence of the salt it is mainly confined within the range of pH 5.5-6.5. In the presence of salts the cation effect is regular in the sense that it follows the lyotropic series and is determined by the order of the electrical adsorption of the cations together with their hydration envelopes. At the comparatively high pH values in the absence of salts the cations are probably adsorbed in a dehydrated condition, which accounts for the irregular or specific cation effect, irregular in the sense that it does not follow the lyotrope series, operating under these conditions. The regular and specific cation effects have been observed with sub-fractions of hydrogen clay having equivalent spherical diameters ranging between specified limits and separated from the same entire clay fraction as also with hydrogen clays after they have been treated by methods aiming at the removal of their free inorganic oxides.

The indefinite nature of the total neutralizable acid goes against the postulate of similarity with weak acids in true solution supported by some workers and invalidates the applicability of the concepts of degree of dissociation and dissociation constant in such systems. Hydrogen clay sols have low values, usually about 5-10 per cent, of the ratios of their free to total acids, that is, of the degree of dissociation in usual language. The potentiometric titration curves of the sols with the alkaline earth hydroxides have, on the other hand, usually a strong monobasic acid character. The inflexion points in the titration curves for these bases almost in all cases lie in the acid region. No second inflexion has been observed even on titrating up to pH 12.

The cation effect also impresses itself on the form of titration curves. The curves with different bases have different forms. While the baryta and calcium hydroxide curves (potentiometric) have a flat initial run and thus have a strong acid character, the caustic soda curves show a comparatively sharp initial rise and in this respect resemble that of a weak acid. The features of the conductometric curves are at direct variance with those of the potentiometric curves. Thus the slopes of the descending portions of the conductometric curves are in the order $\text{NaOH} > \text{Ba(OH)}_2 > \text{Ca(OH)}_2$, indicating a stronger acid character of the NaOH curve compared with the Ba(OH)_2 or Ca(OH)_2 curve.

Sub-fractions of the same hydrogen clay often show nearly the same type of titration curves. The b.e.c. per gramme generally increases with diminishing particle size. Calculated per sq. cm. of the external surface, however, the b.e.c. usually increases with the size of the particles.

When a neutral salt is added to a hydrogen clay sol, both H and Al are exchanged for the cations of the salt. It is only when salts of alkali metal cations are added in very low concentrations, e.g. up to 0.002N, that only H ions are exchanged. The relation between the amount of Al exchanged at a constant pH and the concentration of the added salt is given by a curve which closely resembles the adsorption isotherm.

The conceptions of primary and secondary adsorption of ions, of electrical adsorption and adsorption by valence forces offer a satisfactory explanation of the results recorded in this paper. The interaction between the hydrogen clay and an electrolyte, apart from neutralization and other known chemical processes, involves exchange of H (and aluminium) ions present on the surface of the particles for the cations of the latter. The extent to which the cation will displace these H (and aluminium) ions will depend on the concentration of the added cation and the relative adsorbabilities of the ions. The larger the surface area of a hydrogen clay with alkaline earth hydroxides compared with the same clay with alkali cations compared with alkali metal cations. The adsorption of the cations is determined by their valencies, mobilities and states of hydration. Adsorption is mainly the result of electrostatic forces. When it is brought about by chemical or valence forces, solubility and other considerations become of importance. The regular and specific cation effects, the differences in the shapes of the titration curves with different bases and features of conductometric and potentiometric titration curves, difficult of interpretation in the usual way, find a simple and consistent explanation.

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*STUDIES IN THE PERIODIC PARTIAL FAILURES OF THE PUNJAB-AMERICAN COTTONS IN THE PUNJAB

V. PHYSICAL AND CHEMICAL PROPERTIES OF THE SOILS ASSOCIATED WITH *TIRAK* (BAD OPENING OF BOLLS)

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(With 1 text-figure)

THE idea of investigating the soil conditions in order to determine causes of cotton failures arose as a result of observations made on cotton crop during the cotton seasons of 1935-36 and 1936-37. It was observed that *tirak* or bad opening occurred in one part of the field, while normal plants were found in another part of the same field. It was also found later that *tirak* or bad opening occurred in the same field or in the same portion of a field whenever cotton was grown. These observations suggested that the factors might be associated with *tirak*. This view was also supported by symptoms exhibited by the American cotton plants when they suffered from this physiological disease. Such fields were marked out in the cotton seasons of 1936-37 and soil samples, foot by foot up to a depth of 6 or 12 ft., were taken from these fields or portions of a field where the conditions of plants were found to be normal.

INVESTIGATION

Soils with sodium salts in the subsoil

During the early stages of the soil investigation it was discovered that soils where *tirak* appeared were alkaline varying from pH 9.2 to 9.8. Soils under normal plants were not so very alkaline in reaction, the pH fluctuating between 8.0 and 8.4. But such differences in the pH between the soils where normal and *tirak* plants were observed held good in some cases but not in others. The soil reaction was in the neighbourhood of pH 8.0 even where *tirak* was present (Table I).

Later it was discovered that though the subsoil under *tirak* was alkaline, there were present abnormal amounts of total soluble solids in such soils indicating the presence of neutral sodium salts (Table II). This led to the determinations of total soluble solids in the soils from the normal

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tirak patches (Table II). A complete analysis of the soluble salts, foot by foot, showed that the soils where *tirak* appeared had a subsoil with abnormal amounts of soluble chlorides, sulphates and bicarbonates as compared with the quantities of these salts present in the subsoil where normal plants grew (Table III). The abnormal amounts of sulphates, chlorides and bicarbonates were present from either the third or the fourth foot downwards (Table III).

TABLE I

pH of soils under normal and tirak plants at the Lyallpur Agricultural Farm

Depth in ft.	Sq. 10		Sq. 27 D2		Sq. 27 D1		Sq. 26	
	Normal	<i>Tirak</i>	Normal	<i>Tirak</i>	Normal	<i>Tirak</i>	Normal	<i>Tirak</i>
1 . .	8.1	8.6	8.1	8.1	8.2	8.2	8.2	8.2
2 . .	8.2	9.6	8.0	7.9	8.1	8.1	8.0	8.3
3 . .	8.2	9.7	7.8	8.1	8.2	8.0	8.2	8.1
4 . .	8.3	9.7	8.0	8.7	8.3	8.0	8.1	7.9
5 . .	8.4	9.7	8.1	9.4	8.7	8.0	8.1	8.1
6 . .	8.4	9.6	8.1	9.6	8.8	7.9	8.1	8.3

In some cases there were also present small amounts of sodium carbonate, while it was absent in other cases. This explained the fact that the subsoils under *tirak* plants were more alkaline in reaction in some cases than the subsoils under normal plants, but this difference did not hold good in other cases.

The mechanical analysis of the soils under two types of plants showed that the sand fraction decreased while the clay and silt fractions increased in the subsoil of *tirak* patches, while that was not the case with the subsoil of the normal patches. This difference did not hold good in all cases, as for instance in the case of light sandy soils which are saline in the subsoil. When the soil samples up to 12 ft. depth were analysed it was sometimes found that the sand was at a lower depth in the case of normal soils than in the case of soils with salts in the subsoils (Table II).

TABLE II
Physical and chemical properties of soils under normal and tirak plants

Depth in feet	Normal (sandy loam)					Tirak (sandy loam)					Normal (light sandy)					Tirak (sandy loam)				
	Clay (per cent)	Silt (per cent)	Sand (per cent)	Total solids (per cent)	pH	Clay (per cent)	Silt (per cent)	Sand (per cent)	Total solids (per cent)	pH	Clay (per cent)	Silt (per cent)	Sand (per cent)	Total solids (per cent)	pH	Clay (per cent)	Silt (per cent)	Sand (per cent)	Total solids (per cent)	pH
1	16	20	63	0.054	8.3	23	21	53	0.053	8.3	15	15	68	0.043	8.5	19	22	54	0.059	8.3
2	18	22	59	0.048	8.4	27	22	48	0.053	8.3	15	15	66	0.037	8.4	27	20	52	0.058	8.5
3	19	21	58	0.047	8.4	26	24	47	0.206	8.1	15	18	65	0.041	8.3	30	27	43	0.132	8.7
4	19	22	57	0.043	8.3	26	28	42	0.332	8.1	16	19	61	0.040	8.4	32	28	30	0.315	8.3
5	19	25	50	0.056	8.4	26	24	41	0.250	8.5	15	23	54	0.046	8.3	35	28	36	0.363	8.4
6	21	30	36	0.065	8.3	26	28	35	0.241	8.2	11	21	59	0.036	8.4	34	30	35	0.517	8.7
7	18	37	32	0.084	8.3	28	33	25	0.630	8.3	8	11	77	0.029	8.2	40	25	30	1.157	9.1
8	15	28	49	0.050	8.6	22	44	22	0.552	8.6	5	8	84	0.026	8.3	39	30	21	0.756	9.1
9	7	8	82	0.045	8.7	19	46	22	0.492	8.6	5	8	85	0.027	8.2	32	30	28	0.434	9.0
10	6	6	85	0.047	8.8	11	24	59	0.215	8.0	5	8	83	0.025	8.3	35	35	20	0.424	9.0
11	4	4	89	0.043	8.8	5	5	87	0.061	8.5	4	6	85	0.031	8.2	40	35	12	0.402	9.0
12	4	4	90	0.022	8.8	5	6	89	0.073	8.5	4	8	83	0.030	8.2	27	41	21	0.386	8.8

TABLE III

Quantities of soluble carbonates, bicarbonates, sulphates and chlorides in gm. in 100 gm. of soil (calculated as sodium salts) in normal and tirak patches

Depth ft.	Normal					Tirak				
	Total soluble salts	Carbo- nates	Bicar- bonates	Chlo- rides	Sulphates	Total soluble salts	Carbo- nates	Bicar- bonates	Chlo- rides	Sul- phates
0-084	0-008	0-008	0-009	0-001	0-0048	0-115	Traces	0-101	0-004	0-012
0-087	0-002	0-002	0-001	0-001	Nil	0-116	Do.	0-090	0-001	0-024
0-084	0-001	0-001	0-000	Nil	Nil	0-121	0-002	0-100	0-003	0-021
0-078	Traces	0-001	0-003	0-010	0-010	0-215	0-002	0-189	0-023	0-055
0-082	"	0-072	0-005	0-010	0-010	0-345	0-012	0-182	0-047	0-112
0-078	"	0-066	0-004	0-011	0-011	0-448	0-023	0-202	0-076	0-154
0-043	Nil	0-035	Nil	Nil	Nil	0-073	Nil	0-050	0-007	0-015
0-037	"	0-034	"	"	"	0-105	"	0-053	0-018	0-024
0-041	"	0-035	0-001	Traces	Traces	0-197	"	0-0881	0-051	0-075
0-040	"	0-034	0-002	Do.	Do.	0-342	"	0-079	0-081	0-191
0-046	"	0-037	0-003	Do.	Do.	0-442	"	0-065	0-079	0-274
0-036	"	0-034	0-005	Do.	Do.	0-330	"	0-064	0-064	0-189

Pits were dug on *tirak* and normal patches of a field and the soil of each was separately collected up to a depth of 6 feet and was placed in six separate pots. Thus each of the six pots contained soil from any one-foot layer of the six one-foot layers of *tirak* patch. Similarly another six pots were filled with soil from any one-foot layer of the six one-foot layers from the normal patch. Seeds were sown in June 1936 in each of these pots. It was found that either the seeds did not germinate or they did not grow further after the seedling stage in the pots which contained soils from either the 4th, 5th or the 6th foot of the *tirak* patch, while the plants grew normally in pots containing soil from the 1st and the 2nd foot. The growth was subnormal in the 3rd foot of the soil. On the other hand, the plants grew normally in the six pots containing soil from normal patch. The abnormal concentrations of the sodium salts proved toxic to the roots in pots containing subsoil layers of the *tirak* patch. This was not unusual, as it was later realized that a similar thing occurred in fields where alkali salts, or *kalar* as is commonly called in the Punjab, was present on the surface. This fact was further confirmed by taking soil samples from a field under cotton where there was a big irregular in outline, where 'no cotton plants' were present due to failure of germination. Surrounding this area there was a zone of stunted and scattered plants. Farther away from the second zone the field had a normal stand of cotton with medium growth. The soil samples up to a depth of 6 ft. were taken from each of these zones and analysed (Table IV). The result revealed the same features discussed above. In the area of no-plants the alkali salts were abnormally high from the 1st foot while they were less in amounts in the zone of stunted plants. They were still less in the region of the normal

TABLE IV
Properties of soils taken from regions of medium and stunted growth and no-plant region

Depth in ft.	Medium growth of plants					Stunted growth of plants					Region devoid of plants				
	Clay (per cent)	Silt (per cent)	Sand (per cent)	Total soluble solids (per cent)	pH	Clay (per cent)	Silt (per cent)	Sand (per cent)	Total soluble solids (per cent)	pH	Clay (per cent)	Silt (per cent)	Sand (per cent)	Total soluble solids (per cent)	pH
1	14	23	51	0.109	8.1	18	22	51	0.318	8.3	17	26	51	0.612	8.2
2	10	23	54	0.103	8.1	23	26	43	0.498	8.3	20	27	44	0.708	8.4
3	6.1	29	54	0.088	8.2	24	25	36	0.768	8.2	20	32	39	0.759	8.4
4	3.6	9	84	0.067	8.3	26	33	26	0.742	8.7	22	35	39	0.850	8.5
5	0.8	12	84	0.071	8.2	26	42	23	0.708	8.7	22	46	17	0.804	8.4
6	0.7	9	88	0.050	8.2	20	37	31	0.576	8.7	21	44	20	0.840	8.4

stand of crop of medium growth. The mechanical analysis of the soils showed that the subsoil was sandy under normal stand of crop and heavy in the zones of scattered plants and devoid of plants.

It may be here pointed out that the soils of the Punjab are known to be very heterogeneous and the physical and chemical properties of the soils differ widely even in the same field measuring an acre. It is also found that the concentrations of alkali salts varied greatly in soils taken from two spots situated at a distance of a few feet (Table V).

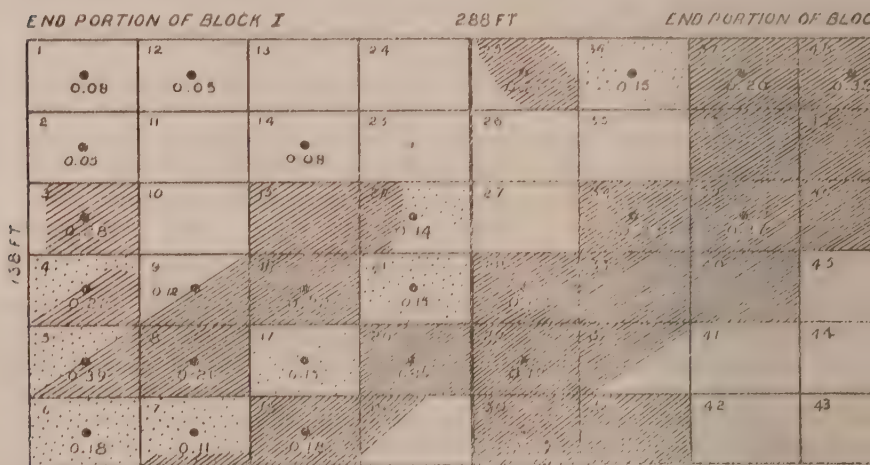
TABLE V

Percentage of soluble salts under normal and tirak plants found in the same field

Depth in ft.	Lyallpur						Sargodha		Montgomery	
	Normal	<i>Tirak</i>	Normal	<i>Tirak</i>	Normal	<i>Tirak</i>	Normal	<i>Tirak</i>	Normal	<i>Tirak</i>
1 . . .	0.077	0.105	0.051	0.076	0.084	0.115	0.055	0.064	0.078	0.078
2 . . .	0.079	0.108	0.045	0.078	0.087	0.116	0.063	0.050	0.065	0.098
3 . . .	0.083	0.219	0.051	0.629	0.084	0.121	0.068	0.147	0.078	0.192
4 . . .	0.069	0.330	0.052	0.591	0.078	0.215	0.059	0.234	0.086	0.198
5 . . .	0.057	0.380	0.045	0.382	0.082	0.345	0.067	0.364	0.078	0.456
6 . . .	0.074	0.390	0.028	0.148	0.078	0.448	0.067	0.242	0.065	0.420

An idea of soil heterogeneity could be obtained from Fig. 1. A field measuring about one acre was selected for an intensive study of the soil conditions as *tirak* was found to occur in patches in 1936. The patches of *tirak* plants and normal plants were found irregularly distributed over the whole acre. The field was therefore divided into 48 small plots of 1/80 acre each and the soil samples were collected from these plots up to a depth of 6 feet. The soil samples were analysed for total soluble salts, physical structure, pH and soluble calcium and sodium. Cotton was sown in these plots in 1938 season and detailed observations on the condition of the crop were made throughout the season. These observations on the growth of the crop will be discussed elsewhere. It was found that normal and *tirak* conditions of the crop in each plot were associated with normal and abnormal concentrations of sodium salts in the subsoil. Fig. 1 has been prepared on the basis of normal and *tirak* condition of the crop as actually observed (unsown interstrips between the plots are not shown). It was sometimes found that normal plants occurred in one portion of the plot, while *tirak* plants occurred in another part of the same plot. So, fresh soil samples were collected to see the condition of the soil under each type of crop and the above-mentioned relationship was found to exist. When *tirak* crop is indicated in a plot in Fig. 1, it does not mean that the whole crop was *tirak* in the entire plot in all cases. There may be normal plants in some of these plots but the majority of plants had shown *tirak*. The intensity and spread of *tirak* was also found to vary in these plots in different years. In 1938 cotton season, the *tirak* appeared in a less intense form and was on a smaller area than in 1939. This difference will be explained later.

The total salts were measured only in this particular case by dionic test for the sake of rapidity, but some of the results were also verified by the direct method. Both the methods revealed high concentrations of soluble salts in *lirak* soils from the 3rd foot and low concentrations of soluble salts in normal soils at all depths.



[Unshaded area indicates normal crop; shaded area indicates *tirak* crop; dotted area indicates partly *tirak* crop; unsown interstrips not shown; ● indicates the place where the soil was analysed]

The above-mentioned facts were again and again confirmed from fields in the different cotton-growing districts in the Punjab where *tirak* was observed in the cotton seasons of 1937, 1938 and 1939. One-foot soil samples were collected from *tirak* and normal patches from the Sargodha, Montgomery, Multan and Lyallpur districts. From each *tirak* patch which may vary in area from place to place, three to six bores were taken. On analysing the samples it was found that at some places the soils of all the three bores from a *tirak* patch contained abnormal quantities of soluble salts in the subsoil. From the results shown in Table VI it will be seen that the total soluble salts were above normal from either the 3rd, 4th or the 5th foot downwards (Table V).

TABLE VI

Total soluble salts in the three bores of tirak patch
(Gm. per 100 gm. of soil)

Khanewal bore No.			Montgomery bore No.			Sargodha bore No.		
I	II	III	I	II	III	I	II	III
0.072	0.072	0.090	0.078	0.080	0.084	0.074	0.072	0.066
0.102	0.068	0.076	0.120	0.114	0.086	0.142	0.074	0.063
0.179	0.084	0.081	0.204	0.234	0.090	0.288	0.078	0.063
0.234	0.126	0.093	0.288	0.300	0.108	0.408	0.108	0.078
0.324	0.222	0.122	0.288	0.312	0.228	0.612	0.360	0.108
0.318	0.444	0.300	0.300	0.414	0.492	0.612	0.396	0.228

It was also found that two bores out of three within a small *tirak* patch of about 1/12 acre or less contained slightly more than normal quantities of soluble salts, while the third bore contained abnormal amounts of total salts. This is an important fact which is found helpful in explaining the greater spread of *tirak* in the same field in certain years than in others.

It was pointed out above that when the soluble salts were high and abnormal in the subsoil of a *tirak* patch, they were preponderantly sodium salts while calcium salts were in smaller proportions than sodium salts. A large number of determinations of sodium and calcium were made in the water extracts of soils from *tirak* patches and in all cases soluble sodium was found to be in larger amounts than calcium (Table VII).

TABLE VII

Free soluble sodium and calcium in normal and tirak patches
(Gm. per 100 gm. of soil)

Depth in ft.	<i>Tirak</i>		Normal		<i>Tirak</i>		Normal	
	Sol. sodium (per cent)	Sol. calcium (per cent)	Sol. sodium (per cent)	Sol. calcium (per cent)	Sol. sodium (per cent)	Sol. calcium (per cent)	Sol. sodium (per cent)	Sol. calcium (per cent)
	0.004	0.006	0.003	0.011	0.004	0.009	0.004	0.009
	0.012	0.002	0.006	0.008	0.029	0.003	0.003	0.012
	0.042	0.003	0.006	0.010	0.084	0.003	0.002	0.010
	0.065	0.003	0.007	0.010	0.152	0.008	0.002	0.010
	0.106	0.003	0.008	0.010	0.126	0.008	0.003	0.009
	0.125	0.003	0.008	0.010	0.130	0.004	0.006	0.016

The results show that sodium is more than 10 times the amount of calcium present in the water extract of the *tirak* soils, while soluble calcium is in smaller amounts than soluble sodium in the normal soils.

The case is, however, found to be different for the exchangeable sodium and calcium in the clay complex of the *tirak* soils. A study of the exchangeable bases of soils of *tirak* and normal patches revealed that in some cases

the conversion of calcium clay to sodium clay in the subsoil of the *tirak* patches had occurred, while it was not the case in other *tirak* patches, even soluble sodium was found to be in higher amounts than soluble calcium (VIII). In the case of normal soils exchangeable sodium was nil or nil and soluble salts were mostly calcium salts. It may be pointed out that the following results exchangeable sodium plus potassium are given. A separate determination of exchangeable potassium revealed that it fluctuated between 0.2 and 0.5 milli-equivalents per 100 gm. of soil, normal as well as in *tirak* patches. So, when the value of exchangeable sodium and potassium is higher than 0.5 m.e., it must be taken that the exchangeable quantity represents exchangeable sodium alone.

TABLE VIII

Exchangeable sodium+potassium and calcium in normal and tirak soils
(M. e. per 100 gm. of soil)

Depth in ft.	<i>Tirak</i>		Normal		<i>Tirak</i>		Normal
	Exchangeable Na+K	Exchangeable Ca	Exchangeable Na+K	Exchangeable Ca	Exchangeable Na+K	Exchangeable Ca	Exchangeable Na+K
1st . . .	0.99	7.4	0.56	5.8	1.4	7.8	0.9
2nd . . .	0.73	8.6	0.25	7.0	2.4	8.4	0.9
3rd . . .	0.43	8.6	0.26	6.8	3.4	6.6	0.6
4th . . .	0.43	8.0	0.30	8.0	2.4	8.0	1.0
5th . . .	1.17	8.4	0.30	6.6	5.4	6.4	0.4
6th . . .	0.78	8.6	0.30	7.1	5.4	6.2	0.6

The degree of sodiumization of clay, i.e. the amount of exchangeable sodium, was not found to bear any relation to the total soluble sodium present. In many cases even though the total soluble sodium salts were high the exchangeable sodium in the clay complex was low, while the amount of exchangeable sodium was high in soils containing lesser amounts of total sodium salts (Table IX).

Thus, the soils where *tirak* appears are found to contain smaller amounts of total soluble solids in the subsoil from the 3rd or the 4th foot downwards. The soluble solids contain larger quantities of free sodium than calcium. In some cases sodium has replaced calcium in the clay complex, in other cases similar base exchange has not taken place even though sodium is found to be in excess of calcium. Except for the above-mentioned differences, the soils from *tirak* patches were not found to differ in character.

A large number of results collected from soils of different fields in different districts where *tirak* was noticed are available in support of the above conclusions.

TABLE IX

soluble and exchangeable sodium and calcium in tirak and normal soils*

Depth in ft.	Sargodha					Lyallpur				
	Total solids (per cent)	Soluble Na (per cent)	Soluble Ca (per cent)	Ex-changeable Na+K (m.e.)	Ex-changeable Ca (m.e.)	Total solids (per cent)	Soluble Na (per cent)	Soluble Ca (per cent)	Ex-changeable Na+K (m.e.)	Ex-changeable Ca (m.e.)
(a) Tirak patches										
0-063	0-003	0-008	1-05	9-4	0-037	0-003	0-008	0-9	9-8	
0-058	0-008	0-007	0-88	11-2	0-076	0-029	0-006	1-1	11-6	
0-140	0-014	0-005	2-12	9-2	0-497	0-148	0-047	NH	11-2	
0-235	0-059	0-004	3-00	7-21	0-583	0-155	0-039	"	9-2	
0-304	0-062	0-008	2-12	6-8	0-581	0-167	0-029	"	7-8	
0-242	0-060	0-005	1-85	6-0	0-375	0-148	0-013	4-2	5-6	
(b) Normal patches										
Sargodha					Montgomery					
0-055	0-003	0-014	0-60	10-6	0-080	0-003	0-010	0-8	6-6	
0-063	0-003	0-012	0-48	12-4	0-098	0-002	0-009	0-8	7-0	
0-068	0-003	0-015	0-54	13-4	0-086	0-001	0-008	0-6	7-6	
0-058	0-003	0-013	0-65	12-6	0-094	0-002	0-009	0-4	8-4	
0-067	0-004	0-015	0-48	12-6	0-098	0-001	0-008	0-6	8-4	
0-067	0-003	0-013	0-43	10-3	0-094	0-001	0-008	0-6	7-2	

*Exchangeable potassium is generally 0-2—0-5 m.e.

It was pointed out above that out of three bores taken on a *tirak* patch one bore showed abnormal amounts of total salts, while the remaining two bores contained slightly more than the normal quantities of these salts. The soluble salts were found to vary from 0-1 to 0-15 per cent in all the bores of the soil. When these soil samples were further analysed, it was found that, even though the total salts were not abnormally high, there were present larger amounts of soluble sodium than calcium (Table X).

TABLE X

soluble sodium and calcium in soils with medium and low salinity in the subsoil (per cent)

Depth ft.	Total soluble salts	Soluble sodium	Soluble calcium	Total soluble salts	Soluble sodium	Soluble calcium
0-079	0-003	0-007	0-078	0-003	0-007	
0-073	0-003	0-007	0-066	0-003	0-006	
0-074	0-004	0-008	0-054	0-004	0-005	
0-095	0-010	0-006	0-060	0-008	0-004	
0-110	0-016	0-008	0-060	0-010	0-006	
0-106	0-018	0-007	0-072	0-013	0-006	

Thus, it was found that in between the soils which had a high and a low salinity in the subsoil, soils with low or medium salinity were also present. The term salinity is used here and hereafter to indicate that the subsoil contains more of soluble sodium salts than calcium salts or more of exchangeable sodium than exchangeable calcium, i.e. for soils which have a low sodium/calcium ratio as contrasted with a high sodium/calcium ratio in normal soils (without salinity). In a *tirak* patch one may not come across a subsoil which is highly saline over the whole area and some bores may show a subsoil which has a low salinity or no salinity at all. The cotton plants that were seen on such fields or patches were affected in their growth and opening of the bolls according to the nature of the subsoil. It was found that *tirak* and normal plants occurred irregularly distributed in such fields or patches whenever cotton was grown. It was also found that the total yield under *tirak* plants increased in such fields or patches during years of favourable weather conditions. The *tirak* in such years was found to be confined to soils where the subsoil was of a medium salinity. *Tirak* was found to be present in parts of a field, in the cotton season of 1939, where it was not observed before. An entire field may have subsoil with a medium salinity and in such fields *tirak* appeared in some years but in other years the crop was found to be normal. On such soils the equilibrium of the crop on the soil could be upset by warm and dry weather or by inadequate water supply. Any one of these factors can tip the scales off the normal condition and *tirak* condition would result.

The salt tolerance of a plant is known to be affected by temperature. Jones and Powers [1938] have shown that salt tolerance of certain grasses and legumes increased at low temperatures and decreased at high temperatures. It is therefore probable that when the temperatures are high the salt tolerance is decreased and the subsoil of a medium or low salinity may during that period affect adversely the root systems of the cotton plants and cause *tirak* on such soils.

Joseph [1925] working on the soils in Sudan has also reported the presence of high concentrations of alkali salts in the 3rd and the 4th foot. The concentration of alkali salts which according to him consisted mostly of sulphates and carbonates in these layers was about 0.3-0.4 per cent; while in the 1st and the 2nd foot it was less than 0.1 per cent. The main difference between the soils in Sudan and the soils in the Punjab are in their clay content, the alkalinity and chlorides. The clay content in Sudan soils is about 40 per cent and the pH is about 9.3. The chlorides, on the other hand, are lower in Sudan than in the Punjab soils. The same author tried to show that the salt contents were inversely related to yields, but an examination of his results did not justify that conclusion. Some of his high-yield plots showed low percentage of salts, while some low-yield plots showed low percentage of salts. It is therefore likely that the soils in Sudan are as heterogeneous as the soils here and soils with low and high salinity are intermixed as they are in the Punjab.

The development of *tirak* on soils with saline subsoil was also found to depend on other soil conditions, the most important being the physical texture of the soil. A medium salinity in the subsoil was enough to produce *tirak* on lands which were light sandy, while *tirak* did not occur under similar conditions

the soil was sandy loam with a higher percentage of clay and silt except under abnormal conditions of weather or water supply. High salinity in the subsoil in a light sandy soil produced the worst form of *tirak* as the toxic effect of sodium on the roots was very high under such conditions. In light sandy soils smaller amounts of sodium either in the soluble or exchangeable form was found to produce a *tirak* crop, while in heavier types of soils *tirak* did not occur under similar conditions.

Similar observations have also been made by Harris [1920], Headley, Curtis and Seofield [1916], Harris and Pittman [1918] and Kearney and Seofield [1936]. Kearney and Seofield [1936] found 0.2 per cent of total salts toxic to alfalfa in sandy soils, while larger amounts were needed to produce toxic effects in loamy soils.

The toxic effect of sodium salts would also depend on the nature of the sodium salt present. Generally sulphates, chlorides and bicarbonates of sodium were found to be present, but the relative proportion of each was found to vary in different soils. The chlorides are known to be more toxic in their effects than sulphates and bicarbonates, and therefore the adverse effect on the crop produced by these salts would depend on the relative amounts of these salts present and their total quantity.

There is a definite indication in the work done on the effect of alkali salts on the growth of plants that chlorides are more toxic than sulphates or bicarbonates. It is pointed out by Harris [1915] that the acid radicals, i.e. the anions, determine the toxicity of alkali salts and not the cations, and the chloride ion has been found to be most toxic amongst anions, while the sodium was the most toxic amongst cations. He has shown that toxicity of sodium chloride was highest amongst the soluble salts in the soil. Voeleker [1916] has also found that sodium chloride was most toxic if present in concentrations of 2 per cent, i.e. $2\frac{1}{4}$ tons per acre.

It is also known that limit for toxicity for different sodium salts for a plant is different. Hilgard [1906] has determined the range at which each sodium salt proves toxic. They are 0.1-0.25 per cent for carbonate 0.3-0.5 per cent for chloride and 0.5-1.0 per cent for sulphate. Hibbard [1906] has shown that much smaller amounts than those may prove injurious to some plants, but there is an agreement that sodium sulphate and sodium bicarbonate are less injurious than sodium chloride and sodium carbonate.

The analysis of the water extract from the *tirak* patches showed that chlorides were always high in the subsoil of *tirak* patches, while they were always very low in the subsoil from normal patches. In normal soils the soluble salts consist mostly of bicarbonates which are salts of calcium and not of sodium. As sodium carbonate was generally absent in *tirak* soils, the toxic effect on the cotton plant might be due mainly to sodium chloride as sodium sulphate and bicarbonate were known to be the least toxic sodium salts. It will be shown in a later contribution that sodium chloride has been found to be more toxic to cotton than either sodium bicarbonate or sodium sulphate.

The presence of salinity in the subsoil was found to depend under irrigated conditions on the depth of the soil crust, i.e. on the depth at which sand layer was present. In some cases it was noticed that, while the upper 6 feet contained normal amounts of total soluble salts, high concentrations of total soluble salts were found to be present at greater depths than 6 feet. The mechanical

analysis of the soil revealed that the percentage of sand increased from the surface to 63 per cent at 7 feet downwards. It appeared that though soluble sodium salts were present in the upper soil crust, irrigations washed them down gradually to the lower layers of sand. The presence of sand prevented the salts from rising up and the salts got gradually washed down to the sand layer. The analysis of such a soil is given in Table XI.

TABLE XI

Field showing the accumulation of salinity at the lower sandy depths

Depth in ft.	Sand per cent	Total soluble solids per cent (gms.)	Soluble Na (mg. per 100 gm.)	Soluble Ca (mg. per 100 gm.)	Exchangeable Na + K in m.e.	Exchangeable Na in m.e.
1st	50	0.0471	11.1	7.5	2.4	8.1
2nd	48	0.0455	9.4	7.1	1.8	9.2
3rd	44	0.0511	8.1	7.9	1.6	7.5
4th	36	0.0550	12.0	5.0	1.4	5.4
5th	46	0.0791	12.0	5.4	1.8	2.2
6th	54	0.0621	11.3	4.6	0.4	2.2
7th	63	0.1296	24.5	4.0	0.6	2.6
8th	68	0.1516	33.2	4.8	0.8	3.0
9th	80	0.1601	36.5	6.2	0.7	4.5
10th	89	0.1145	19.6	4.5	0.5	3.0
11th	87	0.0796	11.8	3.4	0.4	2.4

The results showed that the percentage of sand rose to 63 in the 7th foot and it began increasing downwards from that layer. The total soluble solids were higher in the lower layers of sand than in the upper layers of the soil. Even though the total soluble salts in the soil crust were normal, so much sodium was present in larger amounts than calcium in these upper layers of the soil. The ratio of exchangeable sodium to calcium was also low indicating that while the salts were washed down base exchange had occurred and so much clay was produced. Worst form of *tirak* was observed in this field in 1934. The soil samples were collected from different spots in this area and one sample showed high concentrations of the soluble salts in the first 6 feet, indicating that sodium salts were not washed down by irrigations in some portions of the field.

It should be clear from above that the relations between salinity in the subsoil and *tirak* were complex and a study of the crop was necessary along with the study of the soil conditions. This relationship between salinity and *tirak* was correctly visualized after a great amount of detailed work both in the laboratory and the field. The heterogeneity of the soil in the same portion

tirak patch had added to the difficulty as all the bores from a patch did not indicate the same degree of salinity in the subsoil. It is therefore necessary that soil samples must be taken while the crop is standing, otherwise very great confusion may arise on account of the heterogeneity of the soil.

SOILS WITH NITROGEN DEFICIENCY

The soils where the crops showed symptoms of nitrogen starvation and poor opening of the bolls were found to be light sandy soils containing a large proportion of sand varying from 55 to 70 per cent. The symptoms exhibited by the plants that suffered from *tirak* on soils with saline subsoils resembled in many ways the symptoms that developed in the plants that suffered from lack of nitrogen at the flowering stage and crops which suffered from *tirak* due to nitrogen deficiency could not be distinguished in the early stages of this investigation from the crops which suffered from *tirak* on soils with saline subsoil. It was also found that in some fields crops suffered from *tirak* due to both the causes.

The soils where nitrogen deficiency occurs are normal soils containing normal amounts of soluble salts which are mostly salts of calcium, while the amount of sodium either in soluble or in exchangeable form is nil or negligible (Table XII). The plants make normal growth till August when the leaves begin to turn yellow and are shed. The bolls are few and small containing small seeds. Generally the seeds are lighter in weight than normal. Application of sulphate of ammonia to such soils was found to remedy *tirak*. The relation between nitrogen deficiency and bad opening of the bolls has already been described in a previous contribution [Dastur, 1941].

TABLE XII

Physical and chemical properties of light sandy soils with nitrogen deficiency

(Per 100 gm. of soil)

Depth in ft.	Clay (per cent)	Silt (per cent)	Sand (per cent)	Total soluble salts (per cent)	Exchange- able Na+ K (m.e.)	Exchange- able Ca (m.e.)	Sol. Na (per cent)	Sol. Ca (per cent)
t .	11	13	76	0.077	0.8	6.8	0.002	0.006
d .	13	18	65	0.066	0.4	8.6	Nil	0.006
d .	14	20	62	0.060	0.8	8.6	Nil	0.007
h .	15	24	63	0.080	0.6	8.0	Nil	0.008
h .	13	21	58	0.060	0.4	5.0	0.001	0.007
h .	10	19	62	0.060	Nil	3.8	0.002	0.006

It was found that fields with such light sandy soils deficient in n contained patches which had sodium clay in the subsoil. In some ca soluble salts though normal in quantities contained more of sodium sal of calcium salts. Such patches of saline subsoil were found irregularl tered about in light sandy fields with a deficiency of nitrogen. At on a big or a small patch was found to contain sodium clay or higher am soluble sodium salts in the subsoil, while in soil surrounding such a pat have normal subsoil. Such intermingling of normal soil (light sandy soil with sodium clay in the subsoil or with abnormal amounts of salts in the subsoil within a small area was found to occur. The detailed of the crop, the analysis of the soil underneath, the effect of the applica ammonium sulphate on the plants' growth, the chemical analysis of the and the tannin test on the leaves disclosed the nature of the soil con that were associated with *tirak* due to salinity in one case and due to n starvation in the other. The sulphate of ammonia was found to p beneficial effect on the vegetative growth of the plants but was not fo have ameliorative effect on the opening of the bolls when the subsoil co sodium clay or sodium salts in larger proportions than calcium salts.

From what has been stated above it is necessary to distinguish t bad opening that occurs on soils with saline subsoil from *tirak* caused deficiency of nitrogen. It is now possible, by examining the crop in th ing stage, to know pretty exactly if the symptoms of *tirak* were cause deficiency of nitrogen in the soil or not. The application of tannin t another rapid method of knowing the deficiency of nitrogen as explain previous contribution [Dastur, 1941]. Similarly high concentrations of salts in the subsoil could be known by the drooping leaves of the crop o soils. The drooping of the leaves occurred a week after irrigation, and i cases the leaves did not assume normal position in the evening or in the m The leaves turned black green and were gradually shed.

The term *tirak* which is in common use in the Punjab to denote the tion of the American cotton crop on the two soil types is retained her though it is not scientifically correct to do so. There are some differe the symptoms, as well as in the nature of physiological disturbances pr within the plants, under the two types of soils, but these soil conditi so mixed up together even in small areas that it is deemed desirable to d tiate the two soil conditions without differentiating *tirak*.

DISCUSSION

It is quite clear from above that mere collection of soil samples an lysing them would not give any clue to the above established relatio It is not enough to be told by a zemindar that *tirak* had occurred in field. On account of the great heterogeneity that existed in the soil, absolutely necessary to make sure of the exact spots where *tirak* had oc It was necessary to take a number of bores even after the spot was loca the salinity in the subsoil was very variable. Many a time crops whi inadequately irrigated also showed shedding of leaves and badly opene They should not be mistaken for *tirak* as it occurred under saline cond Lack of cultivation may also produce badly opened crop.

It was also noticed that light sandy soils deficient in nitrogen occurred at one end of a line of 2 acres, while soils with a very heavy and saline subsoil occurred at the other end. In one square of land (i.e. 25 acres) all types of soil conditions may be found. It is this intermingling of normal and *tirak* soils in a small area that had so far obscured the soil conditions associated with *tirak*. In a year of favourable season, the cotton crop in a field may show *tirak* only on patches which have a highly saline subsoil, while the crop may be normal in the remaining parts of the field. Consequently *tirak* is not readily noticeable though it is there. But *tirak* becomes noticeable when adverse weather conditions cause *tirak* to spread on the portions of the fields where a medium or low salinity exists in the subsoil. If the soil samples are taken in such a year, it is possible the analysis may only show low salinity in the subsoil and a conclusion may be drawn that there was nothing abnormal.

The heterogeneity of the soil conditions in a small area would render the practical application of any remedial measure to such soils a difficult task. As an instance, heavy irrigations can wash the salts downwards from the feeding zones of the roots but that remedy can only be applied if a square of land is found to be uniformly saline underneath. In the same square, normal land, light sandy land, land with low, medium and high salinity and with the presence of sand layer at varying depths may be found. Heavy irrigations or rice cultivation will therefore produce varying effects on the different soil types. They will wash down the salts at some places but they will also wash down the important nutrients at other places, rendering the soil infertile. This has usually happened on light sandy soils under normal conditions of cropping and irrigation. Similarly, the applications of sulphate of ammonia to a field may give varying responses, varying according to the nature of the subsoil. The crop would be benefitted at places where the soil is light and sandy and non-saline, but no benefit would be derived if the soil is sandy loam with saline subsoil. Sulphate of ammonia will ameliorate *tirak* on light sandy soils with a normal subsoil but will not do so in parts of the field where there are sodium salts in the subsoil.

The heterogeneity of soil renders difficult the task of studying the effects of various manurial treatments on cotton under field conditions. It has been the experience of the Agricultural Department that nitrogenous manures gave different responses in one year or in one field and low and no responses in another year or in another field. The reasons for such varying results obtained could not yet be understood.

The primary cause of this physiological disorder or disease named as *tirak* may be traced to sandy nature of the cotton tracts in the Punjab. The toxic effect exerted on the roots of cotton plants by the levels of concentrations of sodium salts given above would be much less if the clay contents were high. The sandy nature of the soil also promotes very good root growth and consequently shoot growth of the plant in the first three months of the plant's life, and they therefore later suffer either from nitrogen starvation or a water deficit. The experimental evidence to support this view will be described in another contribution on the subject.

It may be argued that the association of a certain soil condition like salinity with *tirak* would not mean that this soil condition was the cause of *tirak*. The following reasons are put forward to support the view that the presence

of salinity in the subsoil was causing the phenomenon of *tirak* in the American cotton plants :—

1. The toxic effects of sodium salts, especially sodium chloride and sodium carbonate, on the growth of plants both wild and cultivated are too well known.

2. Sodium salts were not found to be present in the subsoils where *tirak* did not occur under any condition of weather and under normal conditions of irrigation.

3. The cotton plants do not grow on soils where the alkali salts are present on the surface.

4. It has been possible to reproduce *tirak* as it occurred in nature by artificial applications of sodium salts to the soil where there was original salinity in the subsoil. These experiments on artificial reproduction of *tirak* in fields with normal lands will be described in another contribution.

5. It is now established that the plants on soils with a highly saline subsoil suffer from a disturbance in their water supply at the reproductive stage when the total leaf area has reached its maximum point. This disturbance of the water balance is found to be partially removed by heavy or frequent irrigations in September-October or by reducing the leaf area of the plant by topping. Recourse to sowing cottons a month later than the normal time, on such soils, These experiments will be described in another paper.

So far attempts have been made to establish the relation of salinity in the subsoil with the symptoms of *tirak* or bad opening of bolls in the American cotton plants as that has been the main object of this investigation. The findings, however, raise the important and fundamental question of the origin of salinity in the Punjab soils and of the causes that may be responsible for salinization to occur at one place and not at another place in the same field or in the same square. Nothing is known about this process of salinization; it has occurred in the Punjab soils. It is not understood whether salinization is an up-grade process or a down-grade process and whether the change is from the saline to the non-saline condition or from the non-saline to the saline condition. It is not known whether the sodium salts were present in the soil crust when it was formed or whether they have been produced by weathering or chemical changes brought about under irrigation. It is needless to emphasize the urgency and importance of this knowledge from academic as well as from a practical point of view.

SUMMARY

Tirak or bad opening of the bolls in the Punjab-American cottons is found to occur on two types of soils and the physical and chemical properties of these soils have been investigated along with the properties of the soils where normal crop grows.

The soils where *tirak* occurs are found to contain abnormal amounts of sodium salts (0.2 per cent or more) in the subsoil from the 3rd or the 4th foot downwards. Sodium in the soluble or exchangeable form is found to be higher than calcium. Such soils are found located in an entire field or in patches of the field. Such *tirak* patches are found surrounded by normal

-saline) soils. *Tirak* is found to occur in such patches every time cotton is grown there.

If the quantity of total salts is not high but medium varying from 0.1 to 1 per cent, *tirak* does not appear under favourable conditions of weather and adequate water supply, but it is developed on such spots in years of drought and warm weather or in absence of adequate water supply. The physical structure of the soil, the sodium/calcium ratio and the relative amounts of different sodium salts present are important soil factors that increase or decrease the intensity of *tirak*.

Another soil type where *tirak* occurs is the light sandy land which produces deficiency of nitrogen in the plant at the flowering stage. These soils are otherwise normal and *tirak* can be ameliorated by the application of sulphate of ammonia [Dastur, 1941].

The soils with high, medium or low salinity in the subsoil are found intermingled in the same area. Adverse weather conditions in a certain year bring about a wider spread of *tirak* in a field in that year than in a year of normal or comparable weather.

The light sandy soils may contain normal (non-saline) subsoils or may also contain subsoils with sodium salts or with low sodium/calcium ratio in exchangeable form. If the soil is light sandy with salinity in the subsoil, *tirak* occurs in the most intense form.

All these soil types may be found in the same square (25 acres). One end of a field may have light sandy soil, while the other may have sandy loam with salinity in the soil. The relationship of these soil conditions with *tirak* were established from a study of (1) the growth of the crop in small plots, (2) results of detailed analysis of the soil underneath normal and *tirak* crops, (3) results of mineral analysis of the leaves, (4) the response to the application of sulphate of ammonia and (5) the tannin test.

Sandy loams with a saline subsoil did not respond to applications of sulphate of ammonia, while a light sandy soil without salinity gave a high response to this fertilizer.

Various suggestions are made regarding the methods adopted to establish the relationship between soil conditions and *tirak* for the guidance of future workers.

Experimental evidence to support the view that salinity in the soil is the cause of *tirak* on such soils will be published in another contribution.

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EFFECT OF TEMPERATURE AND TIME ON DRY WEIGHT DETERMINATION OF MANGO PULP

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DETERMINATION of total dry weight in fruits containing a large amount of both sugars and water is beset with considerable difficulties. It has been shown by Archbold [1925; 1928] that the usual method of estimating dry weight by drying at 100°C. does not give a constant weight of apple pulp even after prolonged heating, because at this temperature decomposition of sugar and liberation of volatile compounds are the possible sources of error in having a constant value. Further, it has been shown whether that the sum of sugar, acid and alcohol-insoluble material is greater than the total dry weight obtained, which suggests that this method of dry weight determination in apples is not satisfactory. She has suggested that drying in *vacuo* at room temperature for three weeks or drying at 50°C. at atmospheric pressure is best suited for routine work. But the temperature and the time of drying is required to be determined for the tissue and drying apparatus in use. In view of this the behaviour of dry weights of mango pulp with rise in temperature and with duration of heating was studied, and the results are presented in this paper.

Mangoes (variety Fazli) were collected from a single healthy tree in an orchard at Malda. After peeling of the skin, pulp from the middle portion of the mesocarp was cut into thin slices. The slices from different fruits were thoroughly mixed up and fixed in warm alcohol (95 per cent). Soxhlet extractor was then used for separating the alcohol soluble and insoluble materials. The initial dry weights of the alcohol insoluble residue were obtained by drying over phosphorus pentoxide to a constant weight at the laboratory temperature and of the alcohol soluble material by first removing alcohol in vacuum distillation and then drying it over phosphorus pentoxide. Then the materials were dried for 24 hours at each of the five different temperatures in succession, namely 31°C. (room temperature), and gas oven temperatures of 50°C., 70°C., 90°C., and 100°C. Next the effect of prolonging the time of drying at 50°C. was investigated. Initial dry weight of both alcohol soluble and insoluble portions were obtained by drying over phosphorus pentoxide as before, then the successive periods of 24 hours drying were done at 50°C.

TABLE I

Effect of temperature on dry weight
(Results expressed as percentage of fresh weight)

Sample	Temperature (°C.)	Material		Difference	
		Alcohol-soluble	Alcohol-insoluble	Alcohol-soluble	Alcohol-insoluble
I Green mango	31 (room temperature)	9.770	2.320	0.517	0.00
	50	9.253	2.311	0.677	0.03
	70	8.676	2.279	1.110	0.01
	90	7.566	2.262	0.390	0.00
	100 (for 8 hours)	7.176	2.260		
II Ripe mango	31 (room temperature)	16.130	5.027	0.820	0.03
	50	15.310	4.996	0.600	0.11
	70	14.710	4.883	0.734	0.00
	90	13.976	4.883	0.540	0.00
	100	13.436	4.880		

Table I and Fig. 1 show that the dry weight of alcohol-soluble material markedly falls with rise in temperature in both green and ripe mangoes, while the loss in alcohol-insoluble material is insignificant. The rate of fall in alcohol-soluble material of the green mango rises with temperature except at 100°C. drying where the fall is comparatively small and this is due to the fact that drying at this temperature was continued only for eight hours and also difference in temperature was 10°C. instead of 20°C. With 24 hours drying at 100°C. we might expect a greater loss. The data presented in Table II and Fig. 2 show a parallel behaviour of two samples with different periods of drying. It will be evident that the total loss in alcohol-insoluble material at 50°C. drying for 120 hours is negligible. Hence drying at 50°C. for 24 hours at atmospheric pressure may be safely used for dry weight determination of alcohol-insoluble materials. In the case of alcohol-soluble material the loss after 24 hours' drying at 50°C. is greatest, and then a steady rate of loss is obtained till the total time of drying is 72 hours, after which the rate slows down. This steady rate of loss at this temperature is interesting to note. If simple dehydration was occurring, the rate of loss would continue

inish. It must be due to a reason other than dehydration. The same phenomenon has been noted by Archbold in apples, where a steady fall takes place from 36 to 130 hours drying. She suggested that the juice possibly contains a volatile constituent of high density, which was removed during the drying process. In a later year a volatile polyhydric alcohol, sorbitol, was isolated by Tutin [1925] in apples, and recently in pears by Kidd, West, Griffith and Potter [1940]. Since in mangoes the temperature effect in losing weight of alcohol soluble material has been noted, an attempt was made to isolate sorbitol in the form of an insoluble benzal compound by a method suggested by Kidd, West, Griffith and Potter. Although sorbitol was not isolated, the presence of some other polyhydric alcohol was presumed. The nature of this substance is not known, but attempts are being made to isolate it. An indirect evidence of the presence of it is the highly hygroscopic nature of the alcohol-soluble substance. While weighing even after drying at ordinary temperature the alcohol-soluble material was found to absorb water readily and the higher the temperature used for drying the greater was its hygroscopic nature.

TABLE II

Effect of time of heating on the loss of dry weight

(Results expressed as percentage of fresh weight)

Sample	Temperature (°C.)	Time of drying in hrs.	Material		Difference	
			Alcohol- soluble	Alcohol- insoluble	Alcohol- soluble	Alcohol- insoluble
.	31 (room temperature)	..	18.90	2.164	0.37	0.024
		1—24	18.53	2.140	0.11	0.008
		24—48	18.42	2.132	0.11	0.000
	50	48—72	18.31	2.132	0.07	0.002
		72—96	18.24	2.130	0.03	0.000
		96—120	18.21	2.130		
.	31 (room temperature)	..	16.65	1.750	0.39	0.006
		1—24	16.26	1.744	0.11	0.004
		24—48	16.15	1.740	0.11	0.000
	50	48—72	16.04	1.740	0.05	0.001
		72—96	15.99	1.739	0.03	0.000
		96—120	15.96	1.739		

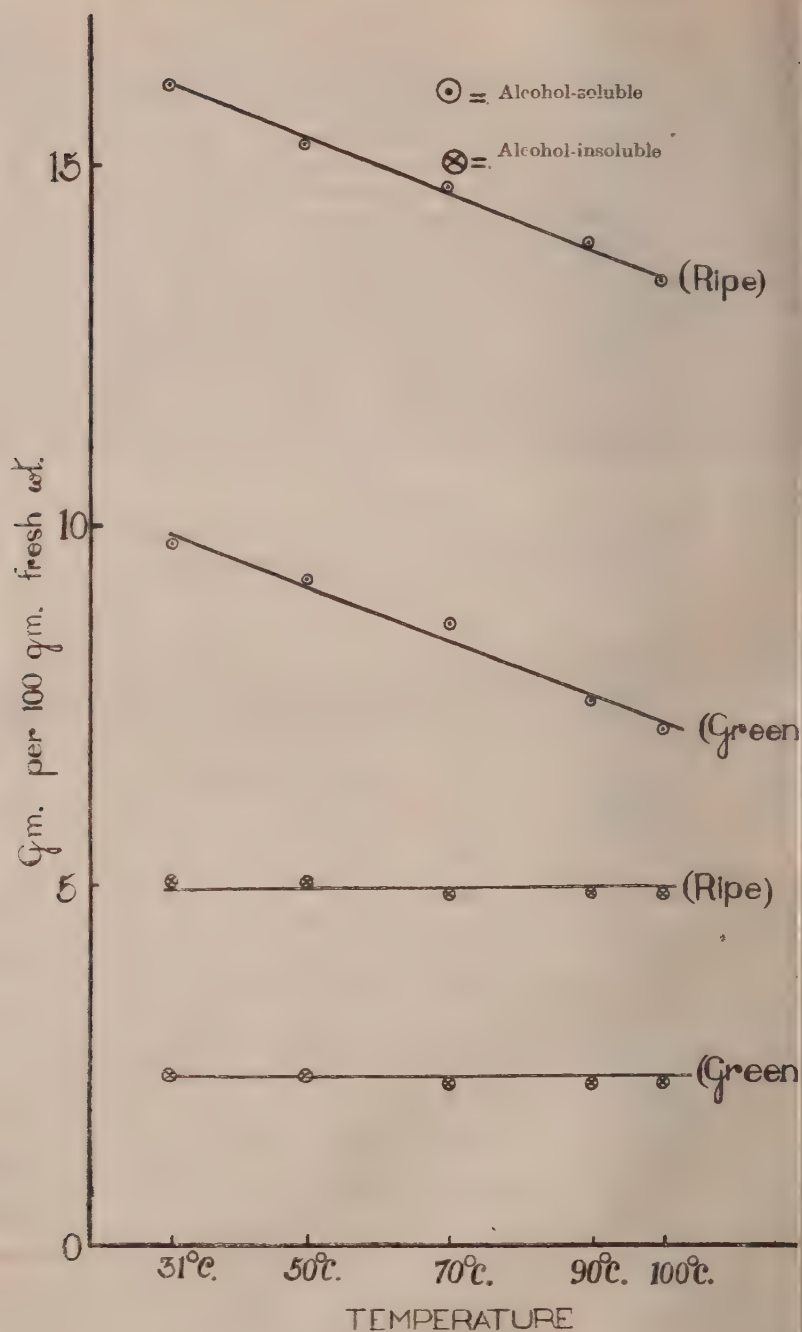


FIG. 1. Effect of temperature on dry weight

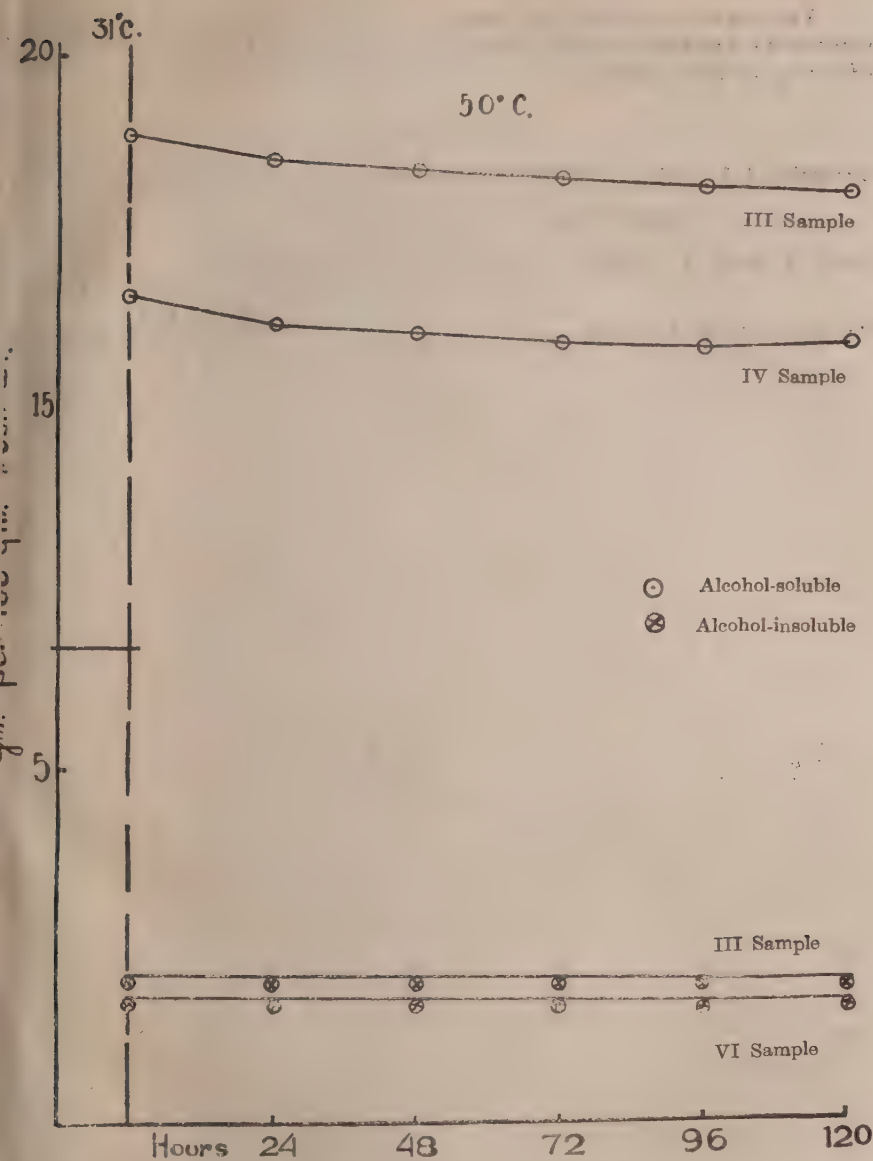


FIG. 2. Effect of time of heating on the loss of dry weight

From this observation it appears that drying at 50°C. for 24 hours at atmospheric pressure is suitable for dry weight determination of alcohol-soluble and insoluble portions of mango pulp. If temperatures higher than 50°C. are employed, there is the chance of loss of a considerable portion of alcohol-soluble material in the form of a volatile compound.

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RIPENING CHANGES IN SOME IMPORTANT VARIETIES OF GRAPES

BY

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(With four text-figures)

In any investigation of the quality of the final product which is influenced by the nature of the raw material, it is desirable to correlate physico-chemical data, as far as is possible, with the quality of the final product. In the drying of grapes and in the preparation of grape juice, for instance, it is important to determine the stage of maturity at which the grapes should be picked to give a high quality product. It was, therefore, thought desirable to make a preliminary biochemical study of the ripening changes in some important varieties of grapes, namely, the Kishmish and the Haitha.

In a study of the relation of maturity to yield and quality, in the case of the Muscat grape used for drying under Californian conditions, Bioletti [1915] pointed out that grapes harvested immature yield not only a smaller total amount of dried product but also raisins of smaller size and of poorer colour and texture. According to Cruess [1938], although it is customary to begin harvesting the Muscat grape for drying in California at about 21° Balling, it is possible to delay harvesting until the grapes have attained at least 25° Balling. The red wine grapes to be blended with the Muscat should be gathered before full maturity in order that the juices may be of higher acidity. Petite Sirah, Alicante Bouschet, Barbera and similar varieties are generally gathered at 18 to 20° Balling. Nichols and Christie [1930], in a study of the dehydration of grapes in California, noticed that, in the case of Thompson grape, the sugar content increased with increase in Balling degree of the juice, while moisture content and acid decreased. In the case of the Muscat grape, however, the sugar content of the raisins made no consistent increase with Balling degree of the juice, although the yield, acid and the weight per raisin showed trends in the same direction as those of the Thompsons. Although their results generally confirmed the conclusions drawn by Bioletti [1915], they pointed out that the differences in yield, observed in the case of grapes from two different districts, might be the result of more favourable climate, soil or crop conditions, for these varieties. Similar results have been observed by the author in a critical investigation of the drying of the Kishmish and the Haitha grapes [Siddappa, 1941].

According to Winkler [1932], except for the work of Bioletti [1925], little or no attempt appears to have been made to determine directly the correlation between the palatability—eating quality—of the analysed fruit and its chemical components such as sugars or acids. Their conclusion was that the Balling

hydrometer test is the simplest and the most reliable that can be used, particularly in determining the degree of ripeness of grapes for the purpose of standardization. According to their data, the Emperor was good when it reached 19° Balling, the Thomson seedless (Sultanina) when it reached 18° Balling and the Malaga and Tokay, when they reached 21° Balling. It will be noticed that these standards are rather low for Kishmish and Bimla grapes, which should attain at least 23 and 20° Balling respectively, to be considered fit for table purposes. The degrees Balling indicated by Bimla and Zion for the varieties named were not, however, accepted by the growers, presumably because they were considered to be too high. Winkler's further showed that the influence of differences in the seasonal temperature on composition and palatability was very similar to that of regional conditions. In cool season, the acidity was relatively high in relation to Balling degree and in hot seasons, it was relatively low, so that in hot seasons, the fruit became palatable at a lower Balling degree than in cool seasons. By combining degree Balling and per cent acidity of the expressed juice in the form of a Balling acid ratio, a highly satisfactory index of maturity was obtained. Table I gives Winkler's standards of maturity for some important table grape varieties.

Myers and Caldwell [1939], in a study of the preparation, by blending, of new types of unfermented grape juices other than Concord juice, give the chemical composition of forty-six important varieties of grapes obtained from the grape variety collection of the United States Department of Agriculture at Arlington Experiment Farm, Arlington, Virginia and the U. S. Horticultural Station, Beltsville, Maryland. Their data are, however, for the hot press juice obtained from grapes harvested when judged to be fully ripe, and do not deal with ripening changes.

MATERIAL AND METHODS

The samples of grapes used in the present investigation were, unless otherwise stated; mostly obtained from the vineyard at the Government Fruit Experiment Station, Quetta, although a few samples of varieties other than the Kishmish and the Haitha were obtained from vine yards situated in Gulistan, Pishin and other districts which specialize in grape growing. At the Fruit Experiment Station, the Kishmish and the Haitha grape varieties, from which the weekly samples were collected during the 1939 and 1940 seasons, are grown by the cane system against wooden supports, although the local practice is to grow them in trenches. In the case of these two important varieties of grapes for which complete data are given, regarding the change in chemical composition during their ripening, the samples were collected at intervals of about seven days, from the very early stages of the fruit set to almost the final stage of ripening, when the berries became yellow and showed signs of decay or deterioration.

Collection of samples

Two vines of each of the two varieties of grapes were marked off in the vineyard, and at intervals of about a week, in the early morning, one or two bunches were picked and brought immediately into the Laboratory for analysis. During the later stages of the ripening, when the grapes were approaching the palatable stage, the bunches were covered with thin muslin bags to pre-

damage by insects. It may be mentioned that no attempt was made to collect weekly random samples for analysis from a large lot of grapes, although, in a few cases, the samples were collected at random from a large consignment of the grapes. The slight fluctuation in the data presented may, therefore, be attributed to the smallness of the samples taken for analysis. Although the work was done during three seasons, to study the seasonal variations, complete analytical data for the last two seasons only are given in this paper.

TABLE I
A suggested standard of maturity for table grapes
(After A. J. Winkler)

Serial No.	Variety	Minimum degree Balling requirement	Balling acid ratios for fruit up to 20° Balling
1	Thompson's Seedless	17	25 : 1
2	Malaga	17	25 : 1
3	Ribier	16	25 : 1
4	Ohanez	17	30 : 1
5	Cornichon	17	30 : 1
6	Muscat	17	30 : 1
7	Emperor	17	30 : 1
8	Tokay	17	35 : 1
9	Olivette Blanche	17	35 : 1
10	Molinera (Red Malaga).	16	35 : 1
11	Rish Baba	16	40 : 1

Percentage of grapes in the bunch

The weight of the bunch was recorded and the berries carefully separated from their pedicels or caps, counted, weighed to the nearest tenth of a gram, and their weight expressed as a percentage of the total weight of the bunch. The percentage of stems and caps was obtained by difference. Any wide variation in the size of the berries, generally in the case of the Haitha grapes, was carefully recorded.

Average weight of 100 grapes

The weight of a grape is a definite index of its size and is easier to determine and far more valuable for comparative purposes than its actual linear or volume measurement. The importance of this type of determination in any

biochemical investigation of ripening changes in fruit and vegetables has been emphasised by Siddappa and Adam [1935] and Adam and Siddappa [1936] in their studies of the ripening of green peas.

The chemical composition, calculated on the basis of analysis of a known number of units, is a far more valuable aid to the visualization of the actual changes that occur during the ripening of the unit, than mere percentages. In a few cases, the standard deviation of the mean for the weight of 100 grapes is also given. The standard deviation of the mean was calculated by using the formula $\sqrt{\frac{\sum d^2}{n(n-1)}}$, in a series of six determinations, choosing at random 100 grapes for each weighing. The weight of the grapes was determined separately after the collection of the day's sample, in order to avoid any considerable variation in the weight, due to respiration, after detaching the bunch from the vine.

Total solids

The figures given under total solids are only comparative, since the determination was carried out on the cold expressed juice, using a Brix hydrometer. As has been previously mentioned in this paper, the Balling or Brix degree of the juice is a valuable index in following up the changes during ripening in the case of the grapes. The Brix value of the juice gives, although not exactly, the percentage of total sugars in the juice, since grape juice contains mainly sugars together with only a small percentage of nitrogenous and other substances, and mineral salts. According to Cruess [1934], however, in grape juice, the Brix or Balling value indicates the total amount of dissolved material in the juice, expressed as sugar, although about 2 to 3 per cent, in most cases, consists of things other than sugar, namely, cream of tartar, tartaric acid, protein, tannin, gums, mineral salts, etc. The Brix values given in this paper are corrected for any temperature difference at the time of their determination.

Yield of juice

While following up the ripening changes, it is highly desirable to determine the percentage of juice in the grapes. For this purpose, one hundred grams of berries were taken and placed in muslin cloth, about six inches square, previously moistened with juice from another lot of grapes under analysis, to prevent loss of yield due to absorption of the juice from the experimental material. Water was not added to moisten the press cloth to avoid any likely dilution of the juice during pressing, as this juice was used for the determination of total solids, acidity, specific gravity, etc. The berries were crushed in the cloth, using a porcelain mortar, and the juice pressed by hand into a beaker. There was a certain amount of loss of juice due to spilling, adhesion, etc. during the process of extraction and its extent, as determined by weighing the pomace from the pressing, was about 6 to 8 per cent, generally. The figures given for the percentage of yield of juice are, therefore, comparative only. The exact percentage of yield will, however, be slightly higher than those given under that head. In all the analyses, the estimation of the yield of juice was carried out by the same individual, using, as far as was possible, the same standard procedure of extraction, to avoid any great variation due to personal factors, such as the amount of pressure used, number of pressings, etc.,

The juice from the determination of the percentage yield was allowed to stand and the clear supernatant liquid taken for titration against standard solution using phenolphthalein as internal indicator. In all the acidity determinations, the settled juice was taken for titration, as the tannin in the fibre, reacts with the alkali. In the case of coloured juices, where phenolphthalein could not satisfactorily be employed as internal indicator, titration was finished using it as external indicator. The figures given for the percentage acidity of the juice are as grams of tartaric acid in 100 c.c. of the juice.

Specific gravity of the juice

During the 1939 analyses, the specific gravity of the juice was determined by weighing accurately 20 c.c. of the juice whose temperature at the time of weighing was recorded. The figures given are not quite exact, as a pipette, instead of a specific gravity bottle, was used to take 20 c.c. of the juice for weighing. The same pipette was, however, used in all the determinations. Weighings were completed, as rapidly as possible, to avoid any wide variation in weight due to evaporation, etc.

Brix-acid ratio

The Brix-acid ratio is the ratio between the Brix reading of the juice and percentage acidity, by volume, as tartaric acid. Although, as has been previously mentioned, the Brix value of the juice is a valuable index in the standardization of the grapes, the Brix-acid ratio appears to be a better index of maturity, as it combines the two important factors responsible for the sound quality of the grapes. High class dessert grapes generally have a Brix-acid ratio which can be fixed fairly accurately for each variety. Grapes that are too rich in sugars or too low in acidity, or *vice versa*, are not generally considered to be suitable for table purposes.

RIPENING CHANGES IN KISHMISH GRAPES

The results of analysis of Kishmish grapes throughout the ripening period are given in Tables III and IV. Fig. 1 shows the relation between the Brix values of the juice and the time of sampling, for the two seasons, namely 1939 and 1940, while the curve for percentage acidity is for the 1939 season only. Fig. 2 shows the Brix-acid ratio in relation to the ripening time. The break in the curves indicates the stage at which the vine, from which the samples were collected was changed.

Effect of season

It will be noticed that the analytical data for the 1939 season, which was a normal year, are more regular and consistent than those for the 1940 season which was marked by abrupt spells of very warm weather during the ripening period. The effect of these sudden changes in the weather is to shift the Brix curve for 1940, slightly above the corresponding curve for 1939, thus indicating an increased photosynthetic activity and consequent accumulation of sugars during those spells of warm and bright weather. The fluctuation of the Brix curve for 1940, indicating the completion, at a very early stage, of the sigmoid curve typical of biological growth, may be attributed to these sudden

bursts of warm weather during the early stages of ripening. The meteorological data for the months of July, August and September for 1939 and 1940 are given in Table II. The effect of season on the Brix value of the juice is therefore, as a shift in the Brix-time curve, warmer weather during the ripening period leading to earlier maturity. In other words, the juice will reach a given Brix value, earlier than in a normal season during a warm season.

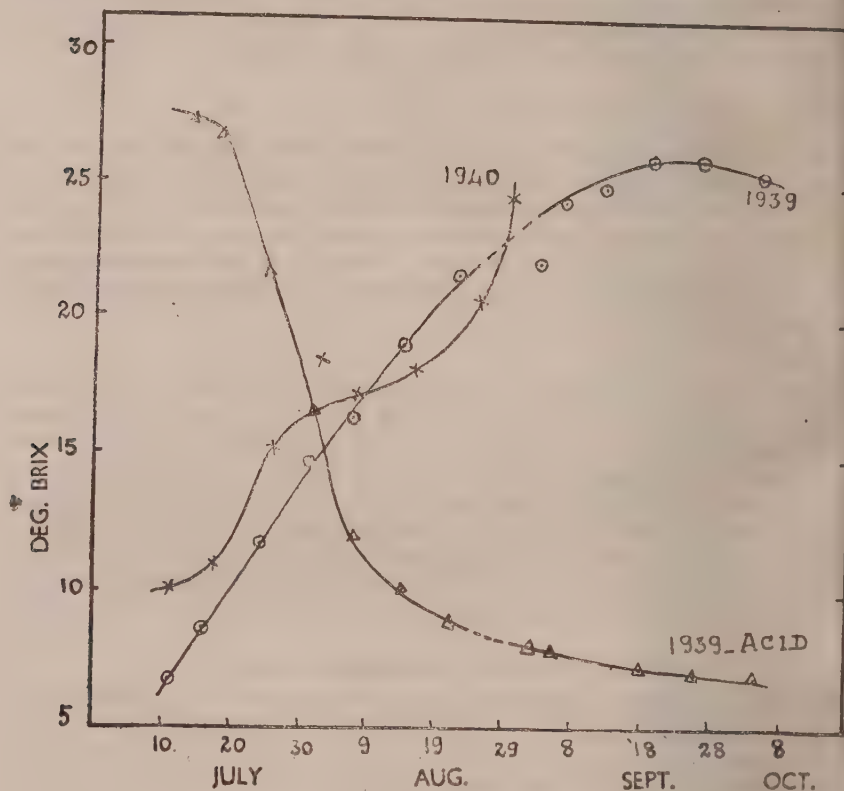


FIG. 1. Brix and acidity changes in Kishmish grapes

Brix value

The Brix-time curve for 1939 is a typical S-shaped one. The Brix of the juice increases steadily throughout the ripening period, reaching a maximum only towards the final stage, when a slight tendency to fall off may be noticed. This may be due either to a slight fall in the sugars through respiration of the grapes, the vine no longer making up for this loss, or it may be due to a certain amount of flow of the solids of the juice back into the vine. The possibility of a slight dilution of the juice, leading to a fall in the Brix value, is, however, excluded, because there is actually a fall in the weight of the grapes as a result of drying up. The utilization of the sugars and other constituents of the juice to build up the non-soluble tissues of the berry, which do not appear in the Brix reading, is another possibility which cannot be ignored.

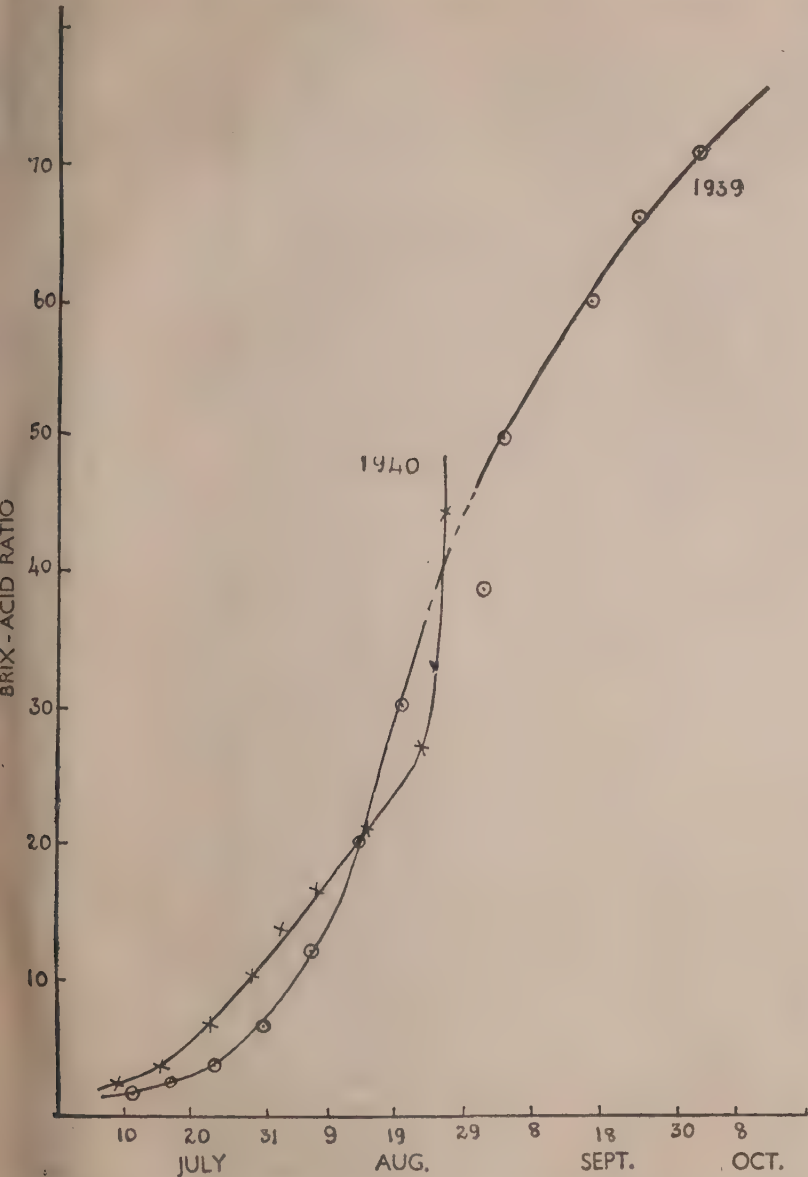


FIG. 2. Brix-acid ratio for Kishmish grapes

Kishmish grapes are considered to be 'eating-ripe' when their juice attains a value of about 23-24° Brix, although, towards the end of the season, the juice may have a Brix value as high as 26-27°. There will be a certain amount of increase in the yield, if the grapes are allowed to attain this degree of ripeness, but this increased yield will not be enough to offset the increased

prices prevailing during the earlier stages of the season. It, therefore, comes a first rate problem to reconcile between these two opposing factors, price and yield. The keeping quality of the crop is another important consideration in any attempt to fix certain definite standards for the proper harvesting of the grapes for table purposes. For drying, however, the grapes should attain at least a Brix value of 23-24°, if the final dried product is of excellent quality.

TABLE II
Meteorological data

Date	July 1939		July 1940		Aug. 1939		Aug. 1940		Sept. 1939		Sept.
	Max.	Min.	Max.	Min.	Max.	Min.	Max.	Min.	Max.	Min.	Max.
1	91	66	95	59	93	56	92	66	93	55	86
2	91	66	96	63	92	54	91	60	94	50	86
3	86	62	98	65	94	59	93	66	92	48	88
4	89	65	97	61	94	57	91	65	92	50	89
5	94	64	95	56	95	63	90	64	94	53	89
6	94	62	95	55	95	66	91	58	93	52	89
7	96	61	95	56	95	59	94	66	94	60	89
8	95	64	95	63	88	62	95	67	92	59	89
9	90	56	95	68	88	63	92	60	92	57	88
10	92	70	95	65	90	55	84	56	90	55	86
11	95	71	96	71	91	52	88	54	88	57	88
12	96	62	96	66	94	57	84	54	84	47	78
13	97	60	95	68	96	63	90	59	80	44	82
14	98	70	96	69	95	64	88	54	79	42	84
15	95	70	96	68	95	65	91	67	84	45	84
16	90	61	94	68	95	63	91	68	86	45	86
17	90	61	94	69	92	59	83	69	87	43	86
18	90	63	95	63	91	55	88	69	86	51	89
19	93	59	95	71	89	55	87	55	85	43	88
20	95	62	94	72	89	50	87	54	86	45	88
21	94	61	91	70	91	53	89	56	87	49	88
22	94	59	95	65	94	55	89	59	87	49	89
23	95	62	95	62	94	59	88	53	85	47	86
24	96	60	90	72	95	61	87	55	83	46	86
25	96	59	92	69	95	69	88	56	83	41	89
26	97	63	92	69	95	68	90	54	83	41	89
27	96	69	95	69	95	67	89	50	87	39	79
28	92	68	92	66	96	67	88	50	83	41	89
29	91	58	95	65	95	64	86	51	84	40	79
30	91	62	96	67	95	64	89	46	83	43	79
31	92	61	93	63	94	57	88	47

Experi- ment No.	Date	Weight of bunch (gm.)	Percent- age of grapes in the bunch	Average weight of 100 grapes (gm.)	Yield of juice (per cent)	Juice		Brix- acid ratio	Remarks
						Total solids (°Brix)	Acidity as tartaric (per cent)		
1	12 July	147	89.8	41.8 ± 1.22	70.0	6.7	4.40	1.5:1	*Juice pressed by the labora- tory attendant, hence the variation
2	17 "	118	92.4	58.8 ± 0.48	57.0*	8.6	4.29	2.0:1	
3	24 "	198	96.0	68.5 ± 0.84	74.0	12.0	3.31	3.6:1	
4	31 "	218	94.0	78.3 ± 0.50	59.0*	15.1	2.32	6.5:1	
5	7 Aug.	302	94.4	106.0 ± 0.50	74.7	16.5	1.40	11.8:1	Still unripe
6	14 "	205	95.6	116.0 ± 1.10	74.7	19.2	0.97	19.8:1	
7	21 "	192	94.8	130	72.7	22.0	0.74	29.7:1	Greenish yellow berries, nearing eating ripe stage
8	2 Sept.	232	95.7	123	71.0	22.0	0.57	38.6:1	
9	5 "	237	95.8	111	69.5	24.7	0.50	49.4:1	Ripe
10	18 "	250	..	120	70.0	26.2	0.44	59.5:1	Fully ripe
11	25 "	315	..	125	75.0	26.5	0.40	66.2:1	Fully ripe
12	6 Oct.	124	..	28.7	0.37	50.4:1	Kandahar grape; fully ripe and yellow

TABLE IV
Ripening changes in Kishmish grapes (1940)

Experi- ment No.	Date	Weight of bunch (gm.)	Percent- age of grapes in the bunch	Average weight of 100 grapes (gm.)	Yield of juice (per cent)	Yield of pomace (per cent)	Juice		Brix- acid ratio	Remarks
							Total solids (°Brix)	Acidity as tartaric (per cent)		
1	11 July	110	91.8	60.0	76.0	21.0	10.0	4.07	2.5:1	
2	18 "	146	93.8	53.0	66.0	30.0	10.5	4.24	2.5:1	
3	25 "	170	93.0	73.0	75.0	16.0	15.1	2.52	6.0:1	Not eating ripe yet. Warm weather
4	2 Aug.	144	93.7	98.0	74.0	14.0	18.5	1.38	13.4:1	Warm weather during the past week. Kishmish grapes from Kandahar are available these days
5	8 "	154	95.5	73.0	79.0	13.0	17.5	1.07	16.4:1	Rather small berries, yellow in colour
6	15 "	139	95.0	89.0	84.0	10.0	18.0	0.86	20.9:1	Nearing eating ripe stage
7	24 "	149	94.0	82.0	78.0	15.0	20.5	0.77	26.6:1	Eating ripe stage
8	28 "	180	96.7	114.0	78.0	12.0	24.5	0.56	43.8:1	Ditto

Acidity

The percentage of acidity falls regularly throughout the ripening period, the fall being rather steep during the early stages and almost flat towards the 'Eating ripe' Kishmish grapes have an acidity of about 0.4 to 0.5 per cent, although in the early stages, when the berries are small, it may be as high as about 4.5 per cent. There is only a very slight fall in the acidity when the eating-ripe stage of ripeness has been reached.

Brix-acid ratio

The Brix-acid ratio is a highly characteristic index of the quality of the grapes. It will be seen, from Tables III and IV and Fig. 2, that it increases steadily throughout the ripening period, changing, during the 1939 season, from 1.5 : 1 to nearly 70 : 1. The variation during the 1940 season was, however, from 2.5 : 1 to 43.8 : 1 only, the ripening changes having not been followed completely, as in the previous season. The curve for 1940 is less regular than that for 1939 due to sudden changes in the weather during ripening. When the grapes are at about the eating ripe stage, the ratio is in the neighbourhood of nearly 40 : 1. Grapes having a ratio far below this are not fit for table purposes, and those that have a ratio far above are generally over-ripe, and, although fit for eating, do not have long storage life. Tentatively, it may be stated, at this stage of our experience, that Kishmish grapes of good dessert quality should have a Brix-acid ratio of about 40 : 1. It may be noted that this ratio for dessert quality Kishmish grapes is higher than that of most Californian grapes (Table I), probably because of their very high sugar content and correspondingly low acidity. Kishmish grapes from Kandahar that are usually sold at Quetta during the peak of the grape season have a Brix-acid ratio of about 50 : 1. They are generally richer both in sugar and in acidity than the ones from Quetta vineyards. The higher Brix reading of the Kandahar grape may be partly due to a slight drying up of the berries during transit and storage, or it may be a function of factors due to variations in soil, climate or cultural practice.

Percentage of berries in the bunch

The percentage of grapes in the bunch increases as the ripening advances, but the change is small. Eating ripe bunches of Kishmish grapes contain about 95 per cent, by weight, of berries, the stems and caps forming about 5 per cent of the total weight of the bunch.

Yield of juice

The yield of juice, as given in the tables, is what is obtained in small laboratory experiments and is comparative only. Under large scale trials, where the bunches are crushed in a grape crusher and pressed in basket presses, the yield of juice from ripe grapes may not exceed about 60—65 per cent, even after two or three pressings. With hydraulic pressure, it may, however, be as high as 70—75 per cent by weight of the fresh grapes.

DEVELOPMENT OF A SINGLE KISHMISH BERRY

It is highly interesting and instructive to trace the development of the various constituents in a single berry throughout the ripening period. The

results of analyses for the seasons 1939 and 1940 are given in Tables V and VI. The total soluble solids in 100 grapes are calculated from the average weight of the berries, the percentage yield of juice and the Brix reading and are, therefore, approximate only. The figures for the amount of acid are deduced in a similar manner. In Table V, however, the acidity has been corrected for the specific gravity of the juice, since the percentage of acidity as given in Table III is on a volume basis only.

It will be noted that the average weight of the berry increases rapidly in the early stages of development and gradually towards the end. The total soluble solids increase in a similar manner, while the acidity decreases continuously, although during 1939, a slight increase is noticed in the early stages. During the very early stages of ripening, the acids accumulate to a certain extent, but towards the last stages, they are readily used up in the synthesis of other constituents.

The total soluble solids-acid ratio is the same as the Brix-acid ratio discussed previously, although it is slightly higher, when the figures for absolute acidity of the berry are corrected for the specific gravity of the juice. The difference between the two ratios increases with the increase in the specific gravity of the juice and hence with advancing state of maturity. In the standardization of grapes, the Brix-acid ratio is, however, more directly and more easily deduced than the total soluble solids-acid ratio.

TABLE V
Development of Kishmish grapes (1939)

Experiment No.	Date	Average weight of 100 grapes (gm.)	Total soluble solids in 100 grapes (gm.)	Acid in 100 grapes as tartaric, corrected for sp. gr. (gm.)	Total soluble solids-acid ratio
1	12 July . . .	41.8	1.96	1.26	1.55
2	17 „ . . .	58.8	2.88	1.41	2.04
3	24 „ . . .	68.5	6.08	1.61	3.78
4	31 „ . . .	78.3	6.97	1.02	6.83
5	7 Aug. . . .	106.0	13.06	1.05	12.44
6	14 „ . . .	116.0	16.63	0.79	21.18
7	21 „ . . .	130.0	20.79	0.65	32.00
8	2 Sept. . . .	123.0	19.22	0.46	41.78
9	5 „ . . .	111.3	19.10	0.35	54.57
10	18 „ . . .	120.0	22.01	0.33	66.70
11	25 „ . . .	125.0	24.84	0.34	73.06

TABLE VI

Development of Kishmish grapes (1940)

Experiment No.	Date	Average weight of 100 grapes (gm.)	Total soluble solids in 100 grapes (gm.)	Acid in 100 grapes, as tartaric, (not corrected) (gm.)	Total soluble solids-acid ratio
1	11 July . .	60.0	4.56	1.86	2.45
2	18 „ . .	53.0	3.67	1.48	2.48
3	25 „ . .	73.0	8.27	1.38	5.99
4	2 Aug. . .	98.0	13.42	1.00	13.42
5	8 „ . .	79.0	10.91	0.67	16.29
6	15 „ . .	89.0	13.46	0.64	21.03
7	24 „ . .	82.0	13.11	0.49	26.75
8	28 „ . .	114.0	21.79	0.50	43.58

RIPENING CHANGES IN HAITHA GRAPES

The results of analyses of Haitha grapes, during the 1939 and 1940 seasons, are given in Tables VII and VIII. It will be noticed that the data are more or less similar to those recorded in the case of Kishmish grapes, although a few minor changes can be seen in some of the items. Although the bunches are larger in size than those of the Kishmish, the percentage of berries is not very different. The average weight of a single ripe berry may be as high as 5 mas. The yield of juice varies from 61.0 to 77.0 per cent throughout the period of ripening. The Brix reading of the juice increases and the percentage acidity decreases, throughout the period of ripening, the curves (Fig. 3) being typically S-like. The Brix readings for 1940 are higher than the corresponding ones for 1939, as in the case of the Kishmish grapes, the differences being due to seasonal factors, as has been explained previously. The slight scatter noticed in the plotted readings both for Brix reading and the percentage acidity may be due to the unavoidable variation in the experimental material itself, the bunches of grapes often containing a large percentage of berries far below the average size. The effect of this natural variation in size in the experimental material was, however, avoided, as much as possible, by rejecting almost all those berries that differed widely from those of average size in the bunch. The Brix-acid ratio (Fig. 4) rises slowly in the early stages of development and more rapidly as the eating ripe stage is being reached, after which the increase is rather less rapid. Under local conditions, Haitha grapes having a Brix reading of about 19° and 0.46-0.47 per cent acidity are considered fit

for eating, although samples of these grapes, from Gulistan and other places have been found to have a juice of about 23.5° Brix and 0.28 per cent acidity. The low Brix reading attained by Haitha grapes may be due to the effect of soil or climate, or it may be due to cultural practice, as has been pointed out elsewhere [Siddappa, 1941]. The Brix-acid ratio of eating ripe Haitha grapes will be about $40 : 1$, although it may be as high as $80 : 1$ in certain cases. This ratio is about the same as for Kishmish grapes, as the Haitha grape is low in its Brix and acidity. During the 1939 analyses, the Brix reading of the juice even on 19 September was only 19° . The grape season ends by the end of September and even if the berries are allowed to ripen still further the Brix value may increase slightly, but the season will become unduly long and uneconomical.

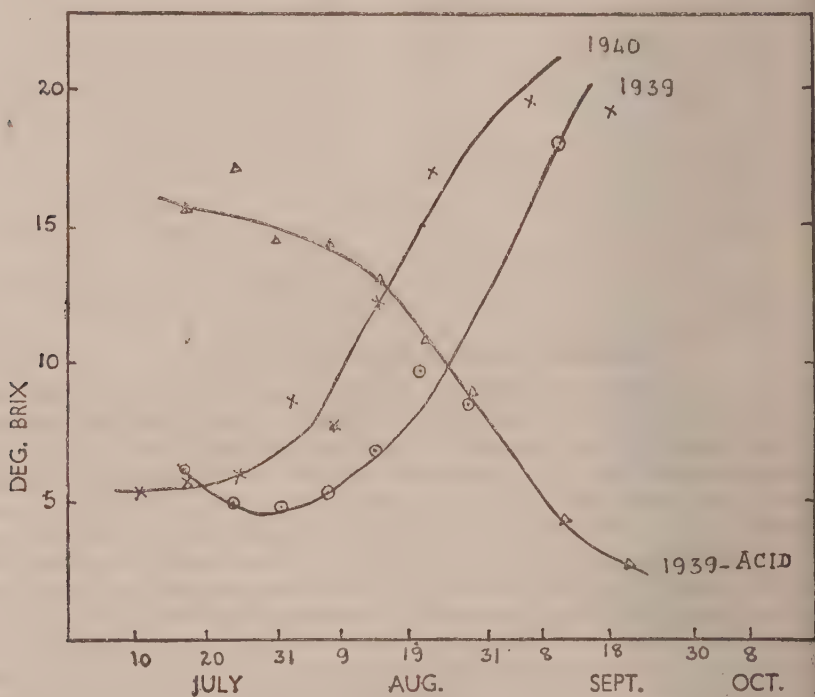


FIG. 3. Brix and acidity changes in Haitha grapes

DEVELOPMENT OF A SINGLE HAITHA BERRY

Changes in total soluble solids, absolute acidity, etc. during the development of a single Haitha berry are given in Tables IX and X. As in the case of the Kishmish grape, the data are calculated on the basis of development of 100 berries. It will be noticed that the results are similar to those recorded in the case of the Kishmish grape, although the figures for total soluble

acidity are comparatively higher due to the naturally bigger size of the grape. The total soluble solids increase and the absolute acidity decreases, throughout the period of ripening under observation. As in the case of the Kishmish grape, there is a slight tendency for the acids to accumulate during the very early stages of development of the berry. The total solids-acid ratio is the same as the corresponding Brix-acid ratio, the stage acidity figures having not been corrected for the specific gravity of juice.

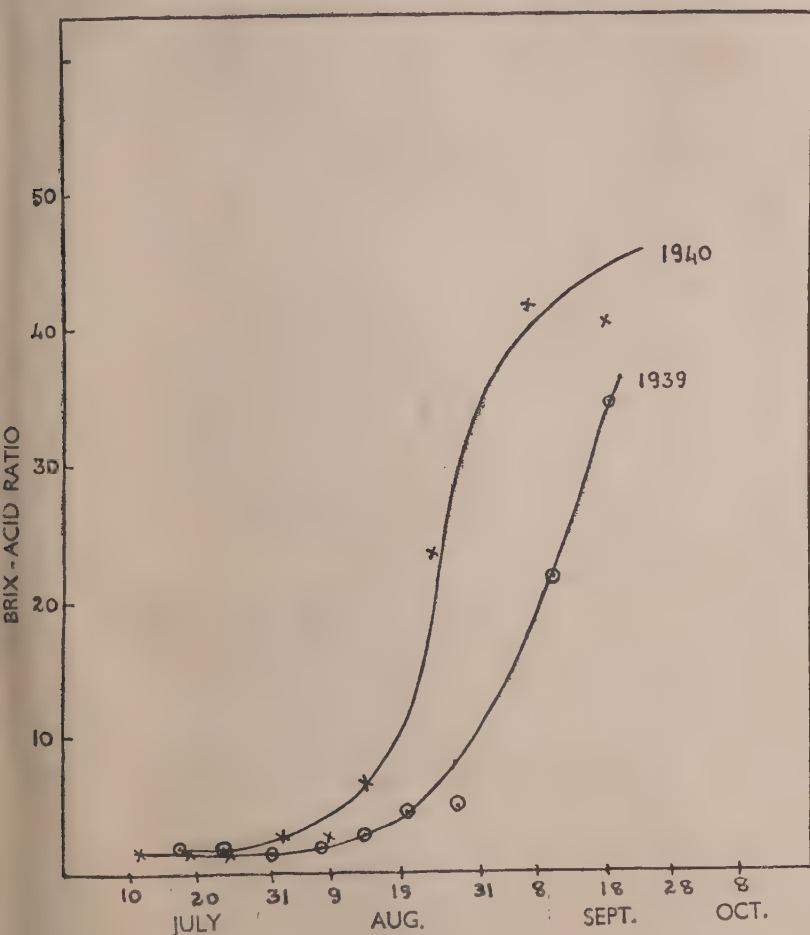


FIG. 4. Brix-acid ratio for Haitha grapes

TABLE VII
Ripening changes in Haitha grapes (1939)

Experi- ment No.	Date	Weight of bunch (gm.)	Percent- age of grapes in the bunch	Average weight of 100 grapes (gm.)	Juice			Brix- acid ratio	Remarks
					Yield (per cent)	Total solids (°Brix)	Acidity as tartaric (per cent)		
1	17 July	257	95.0	169.3 + 4.6	61.0	6.0	3.12	1.9:1	
2	24 "	400	94.8	172.3 + 3.7	70.3	4.7	3.41	1.4:1	
3	31 "	385	92.9	176.0 + 3.8	66.7	4.5	2.92	1.5:1	
4	7 Aug.	468	94.0	186.0 + 3.4	71.3	5.0	2.85	1.8:1	
5	14 "	410	95.6	231.7 + 1.3	74.7	6.5	2.48	2.6:1	
6	21 "	342	87.1	251	74.8	9.2	2.11	4.4:1	
7	28 "	307	92.8	252	72.8	8.0	1.68	4.8:1	
8	11 Sept.	277	95.3	470	71.0	17.7	0.82	21.6:1	Sudden change in Brix-acid ratio
9	18 "	688	..	542	77.0	17.7	0.51	34.7:1	Not yet fit for dessert purposes
10	25 "	Unfortunately, somebody had removed all the bunches from the experimental vines

Experi- ment No.	Date	Weight of bunch (gm.)	Percent- age of grapes in the bunch	Average weight of 100 grapes (gm.)	Yield of juice (per cent)	Yield of pomace (per cent)	Juice			Remarks
							Total solids (°Brix)	Acidity as tartaric (per cent)	Brix- acid ratio	
1	11 July	215	96.3	147	67.0	23.0	5.2	3.34	1.6:1	Juice from whole lot, in- cluding small berries
2	18 "	305	92.5	187	74.0	20.0	5.8	3.53	1.6:1	
3	25 "	263	95.8	172	68.0	20.0	5.7	3.43	1.7:1	Very warm weather. Large number of berries below average size
4	2 Aug.	160	95.6	200	74.0	18.0	8.4	3.04	2.8:1	Warm weather during the past week. Small bunch
5	9 "	{ 115+ 145	93.5	169	73.0	19.0	7.5	3.00	2.5:1	Two bunches were taken
6	15 "	172	95.4	248	78.0	15.0	12.0	1.75	6.9:1	Not yet eating ripe
7	24 "	550	94.9	345	84.0	15.0	16.7	0.71	23.5:1	Numerous small berries in the bunch
8	7 Sept.	525	97.1	510	80.0	12.0	19.2	0.46	41.8:1	Eating ripe stage; green- ish yellow berries
9	19 "	680	..	496	19.0	0.47	40.4:1	Eating ripe stage
10	26 "	All the bunches had been removed by somebody

TABLE IX
Development of Haitha grapes (1939)

Experi- ment No.	Date	Average weight of 100 grapes (gm.)	Total soluble solids in 100 grapes (gm.)	Acid in 100 grapes, as tartaric (gm.)	To sol solid ra
1	17 July . .	169.3	6.20	3.22	
2	24 „ . .	172.3	5.69	4.13	
3	31 „ . .	176.0	5.28	3.43	
4	7 Aug. . .	186.0	6.63	3.78	
5	14 „ . .	231.7	11.25	4.29	
6	21 „ . .	251.0	17.28	3.96	
7	28 „ . .	252.0	14.68	3.08	
8	11 Sept. . .	470.0	59.07	2.73	
9	18 „ . .	542.0	73.87	2.13	

TABLE X
Development of Haitha grapes (1940)

Experi- ment No.	Date	Average weight of 100 grapes (gm.)	Total soluble solids in 100 grapes (gm.)	Acid in 100 grapes, as tartaric (gm.)	To sol solids ra
1	11 July . .	147.0	5.12	3.29	
2	18 „ . .	187.0	8.12	4.88	
3	25 „ . .	172.0	6.67	4.01	
4	2 Aug. . .	200.0	12.43	4.50	
5	9 „ . .	169.0	9.25	3.70	
6	15 „ . .	248.0	23.21	3.39	
7	24 „ . .	345.0	48.40	2.06	2
8	7 Sept. . .	510.0	78.34	1.88	4
9	19 „ . .	496.0	

ANALYSIS OF SOME IMPORTANT LOCAL VARIETIES OF GRAPES

Although the Kishmish and the Haitha are the two most important grapes in Baluchistan, there are a number of other varieties grown on a fairly large scale, in some of the grape-growing tracts of the province. They are generally seeded white grapes, although a few like Tore, Sahebi and Khair-e-ama are black or purplish black grapes. It was, therefore, thought desirable to collect a number of samples of these varieties, especially at the time of harvesting, and find out their Brix-acid ratio, in order to be able to set up some empirical standards of maturity for the profitable harvesting of at least a few of the important varieties of grapes grown in the Province. The results are given in Table XI. It will be noticed that fully ripe white grapes are generally high in sugars and low in acidity, thus giving a comparatively high Brix-acid ratio, while the black grapes from Quetta and Pishin are high both in sugars and in acidity, giving a comparatively low Brix-acid ratio. Sahebi which is a pale purple coloured grape, with seeded oval berries, has a characteristic flavour and is, therefore, highly valued as a table grape. When eating ripe, its juice has a Brix reading of about 20° and an acidity of about 0.5 per cent. Dark purple or black grapes are generally known locally as 'ore and their nomenclature is, therefore, not definite. The highest Brix value recorded in the table, namely, 28.7° was for a sample of Kishmish grapes from Kandahar, and even at this high value, the acidity was as high as 0.57 per cent, giving a Brix-acid ratio of only 50.4 : 1. The superiority of the Kandahar Kishmish grapes, on which popular opinion places a high value, may be partly due to its peculiarly high Brix and acidity values. There is a wide variation in the Brix-acid ratio, namely from about 11 : 1 to 84 : 1, although a ratio of about 40 or 50 to one would be sufficiently accurate to determine the eating-ripe stage of maturity of many of the varieties of grapes for which the data has been collected. The difficulty of fixing, at the present state of our knowledge, more definite standards will, however, be appreciated when one realizes the possibility of the wide variation in the ratio, even at the so-called eating-ripe stage.

ANALYSIS OF SOME IMPORTANT FOREIGN VARIETIES OF GRAPES

At the Fruit Experiment Station, Quetta, a number of important varieties of grapes have been lately introduced and their performance, under local conditions, is under investigation. Samples of grapes from five of these imported varieties were analysed during the seasons of 1939 and 1940 and the results are given in Table XII. It may be pointed out that the berries were considered to be fully ripe at the time of analysis, during both the seasons. The five varieties named, Emperor, Black Hamburg and Gros Colman are all purple coloured seeded grapes, while Olivette Blanche is a seeded white grape. Thompson's Seedless, a small, round, seedless, white grape resembling the Kishmish in several respects. Emperor and Olivette Blanche, both from California, are reputed to be late varieties, eminently suited for cold storage and transport. Thompson's seedless is the most important white grape extensively used for drying in California and elsewhere.

It may be assumed, for the present, that many of these foreign varieties might attain, under local conditions, a Brix value of 19—20° and a Brix-acid

ratio of about 40 : 1, although in the case of Thompson's Seedless, the recorded is only 15·3 : 1, due to the high acidity of the juice. At the tin analysis, the berries of this variety, although ripe and greenish yellow in colour were very small, the average weight of a berry being 0·48 gm. only, the much less than about half the weight of an average Kishmish berry. doubtful if this grape could compete successfully with the popular Kishmish, unless it be for its well balanced sugar-acid ratio.

TABLE XI

Analysis of some important local varieties of grapes (1939-1940)

Serial No.	Date	Variety, etc.	Weight of 100 grapes (gm.)	Juice			Remarks
				(°Brix)	Acidity as tartaric (per cent)	Brix-acid ratio	
1	4-10-39	Kishmish (Quetta)	...	26·2	0·37	70·8 : 1	Ripe; seedless grape
2	6-10-39	Kishmish (Kandahar)	...	28·7	0·57	50·4 : 1	Ripe
3	6-10-39	Do	...	26·1	0·43	60·7 : 1	Ripe
4	19-8-40	Kishmish (Quetta)	92	26·0	0·45	57·8 : 1	Yellow berries
5	19-8-40	Do	...	25·5	0·67	38·1 : 1	Slightly greenish
6	10-9-40	Do	...	24·0	0·48	50·0 : 1	Sample from Experiment Station
7	5-10-40	Do	...	26·8	0·55	48·7 : 1	Over-ripe grapes
8	6-8-40	Kishmish (Kandahar)	174	24·7	0·45	54·9 : 1	Early season sample
9	4-10-39	Haitha (Pishin)	...	23·0	0·23	82·1 : 1	Large white grapes; seeds; ripe
10	23-10-39	Do	...	19·5	0·36	54·2 : 1	Ditto
11	28-9-39	Haitha (Gulistan)	550	23·5	0·28	83·9 : 1	Ditto
12	4-9-40	Haitha (Quetta)	...	17·3	0·52	33·3 : 1	Slightly unripe
13	10-9-40	Do	528	19·5	0·46	42·4 : 1	Ripe
14	8-9-39	Tand (Gulistan)	520	20·5	0·62	33·3 : 1	White grape; full
15	9-9-39	Do	...	22·0	0·67	32·8 : 1	Ditto
16	8-9-39	Kalmak (Gulistan)	370	23·7	0·45	52·7 : 1	Ditto
17	9-9-39	Do	...	22·6	0·52	43·5 : 1	Ditto
18	26-10-39	Khair-e-Ghulama	584	26·2	0·37	70·8 : 1	Dark purple grapes
19	22-8-39	Black Monucca	302	22·0	1·27	17·3 : 1	Dark purplish grapes in acid; ripe
20	9-8-40	Shendukhani	172	24·8	0·68	36·5 : 1	Long seedless Kishmish grape; ripe
21	9-8-40	Sahebi	324	16·7	0·61	27·4 : 1	Large, slightly oval with light purple and marked not fully ripe
22	31-8-40	Do	...	19·7	0·53	37·2 : 1	Ripe
23	19-8-40	Kadak (Quetta)	320	23·1	0·76	30·4 : 1	Large round white berries; seeds thin skin, juicy and sweet taste

TABLE XI—*contd*

Date	Variety, etc.	Weight of 100 grapes (gm.)	Juice			Remarks
			(°Brix)	Acidity as tartaric (per cent)	Brix-acid ratio	
19-8-40	Sheikh Ali	184	13.7	1.23	11.1:1	Slightly oval berries of medium size; white, seeded grape with strongly acid taste; not fully ripe
24-8-40	Do	360	21.0	0.70	30.0:1	Ripe berries
24-8-40	Hussaini	464	18.1	0.81	58.4:1	Large greenish yellow berries resembling the Haitha berries, but differing from them in being uniformly thick, with only a slight concave on one side; very sweet seeded grape; ripe
9-8-40	Tore	244	27.8	0.42	66.2:1	Large slightly oval berries; thick purplish black skin; seeded sweet black grape; ripe
24-8-40	Black grape (Gulistan).	580	22.2	0.70	31.7:1	Large round purple black berries; thick skin; seeds present; acid sweet taste; appears to be different from Tore; ripe
24-8-40	Black grape (Quetta)	560	20.6	0.62	33.2:1	Compact bunch; large round seeded black grape; ripe

SUMMARY

A detailed investigation has been carried out into the changes that take place during the ripening of the Kishmish and the Haitha grapes, two of the important varieties of grapes grown in Baluchistan. The results of studies of a few other important varieties of grapes, local as well as foreign, and the limitations for fixing up definite and exact standards of ripeness have been pointed out. The main results are briefly as follows:—

Kishmish grapes

In the case of Kishmish grapes, the Brix value increases steadily throughout the main period of ripening, although a slight fall may be noticed towards the final stage, when the berry has started to dry up. The percentage of acidity falls regularly throughout the ripening period, the fall being rather towards the early stages and almost flat towards the end. Eating ripe Kishmish grapes have generally a Brix value of 23—24° and an acidity of about 0.5 per cent. Grapes having a considerably higher Brix reading and a lower acid value are considered to be over-ripe and are of poor palatability on account of their ill balanced Brix-acid ratio.

TABLE XII

Analysis of some important foreign varieties of grapes (1939-40)

Serial No.	Date	Variety, etc.	Weight of 100 grapes (gm.)	Juice			Remarks
				(°Brix)	Acidity as tartaric (per cent)	Brix-acid ratio	
1	7-10-39	Black Hamburg	374	21.5	0.46	46.7:1	Large loose large, round, plish black seeds present skin; not full the time of a
	27-10-39	Do	...	19.5	0.70	27.9:1	Ditto
	2-10-40	Do	...	18.0	0.37	48.7:1	Ditto
2	7-10-39	Emperor	354	15.7	0.50	31.4:1	Light purplish slightly oval seeds present attached by thick caps; la of grape re keep long in age; not f under local co
	14-10-39	Do	...	16.8	0.40	42.0:1	Ditto
	27-10-39	Do	...	17.2	0.52	33.1:1	Ditto
	2-10-40	Do	...	19.0	0.68	28.0:1	Juice extracted 'hot' method slight increase reading
3	7-10-39	Olivette Blanche	560	18.0	0.49	36.7:1	} Loose bunches size; long oval thick skin; white grape slightly astr taste; late v white grape; ripe at the th periment, due conditions
	27-10-39	Do	...	16.5	0.56	29.5:1	
	2-10-40	Do	...	14.2	0.54	26.3:1	
4	7-10-39	Gros Colman	480	19.4	0.31	62.6:1	} Purplish black seeds present; ripe at the analysis
	27-10-39	Do	...	17.4	0.37	47.0:1	
5	11-9-40	Thompson's Seedless	48	19.3	1.26	15.3:1	Small loose small, round, white berries; ing acid sweet greenish yel colour; this is foreign grape tensively for ripe berries ra small in size

The Brix-acid ratio is highly characteristic of the grape, and when in conjunction with the Brix reading, serves to fix certain practical standards for the maturity of the grape. Tentatively, a ratio of about 40 : 1 and a minimum Brix reading of about 23° may be used to define Kishmish grapes of dessert quality, although grapes having a higher Brix reading and a lower ratio are not considered to be unfit for table purposes.

percentage of berries in the bunch increases only slightly as the ripeness and the eating-ripe bunches contain about 95 per cent by weight of berries, the stems and caps forming about 5 per cent of the total weight of the bunch.

Under experimental conditions, the percentage of juice in the berries remains practically constant throughout the period of ripening and constitutes about 80 per cent of their total weight, the remaining 20 per cent being made up of skin and flesh.

During a comparatively warmer ripening season, the Brix values are generally higher than the corresponding ones during a normal season, the increase being mainly due to the accelerated photosynthetic activity during periods of bright and warm weather. The changes in the various constituents of grapes during an abnormally warm season are less regular than in a normal season.

During the development of a single berry, its average weight increases rapidly during the early stages and more gradually towards the end. The total soluble solids increase in a similar manner, while the acidity decreases continuously, although there is a marked tendency for the acids to accumulate during the early stages.

Kishmish grapes from Kandahar are generally richer than Quetta ones, as shown by their Brix and acidity values. This may be due to the soil or climatic conditions during storage and transport.

Cultural treatments such as staking, trenching, etc. may considerably influence the changes during the development of the grapes.

Haitha grapes

The changes observed during the ripening of the Haitha grapes are almost similar to those that occur in the case of the Kishmish grapes, except for a greater scatter in the data for the various constituents, due to the inherent non-uniformity of the experimental material, bunches of grapes often containing a few berries far above or below the average size. The Brix reading increases and the percentage acidity decreases throughout the main period of ripening, the Brix readings being slightly higher in an abnormally warmer season than in a normal one. Under local conditions, eating ripe Haitha grapes have a Brix-acid ratio of about 40 : 1 and a Brix reading of 18—20° only. Grapes from other parts have been found to be considerably higher in Brix reading, as a result of climatic conditions, cultural practices, etc.

In the case of the Kishmish berry, during the development of a single berry, the total soluble solids increase and the absolute acidity decreases throughout the ripening period and there is a marked tendency for the acids to accumulate during the early stages.

Other varieties

Other local white grapes like Kadak, Hussaini, Tand, Kalmak, Sheikh, etc., have, when ripe, a Brix-acid ratio widely differing from about 40 : 1, but are generally rich in sugars and low in acidity. Purple-coloured grapes like Basmala and Khair-e-Ghulama are generally rich both in their Brix and acidity and have a comparatively low Brix-acid ratio. Eating-ripe Sahebi-

grape has a Brix acid ratio of about 40 : 1 and, being highly flavoured, considered to be a high class table grape.

Among the foreign varieties of grapes that have been introduced in the Province, Emperor, Gros Colman and Hamburg are purple-coloured, while Olivette Blanche and Thompson's Seedless are white grapes. Under local conditions, they may attain a Brix value of 19–20° and a Brix-acid ratio of about 40 : 1. At Quetta, the Thompson's Seedless is a very small variety with high acidity and low Brix-acid ratio and does not compare favourably with the Kishmish grape.

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RESEARCH NOTE

PRODUCTION OF FLOWERS ON ROOTSTOCK STEMS OF MANGO GRAFTS IN THE NURSERY

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(With Plate XVIII)

appeared to be of much interest, at this station, to note during the 1941 season some cases of flowering from the stem of the seedling rootstock of one-year old mango grafts (inarcheds) which were yet in pots in the nursery. It is not uncommon to see the scion shoot flowering in the first season after grafting. They usually are shoots taken from mature parent trees. But, flowering from rootstock stem is rather unusual. The seedling does not, as a rule, flower before it is at least five to six years old.

The grafts were prepared from mature scion parents of two Bombai, Langra and one Fazli mango trees. The seedlings used as rootstocks were of mixed origin. They were sown during the rains (June and July) 1938 and potted in June, 1940. Inarching was done in July the same year. At the time of inarching the seedlings were 0.75—1.0 cm. in diameter at the base, and 45—50 cm. in height. The grafts were finally separated from the parent trees in October. They were then kept under partial shade in the nursery.

In the spring of 1941, a good many of these grafts flowered from their rootstock shoots. The extent of flowering was rather conspicuous. It is not seen to such an extent. The scion parent trees were also in very early flowering. The summer of 1940 was unusually dry and the trees were in their 'off' year that year. The heavy flowering of the parent trees and the scions taken from them were, therefore, considered to stand to

flowers appearing from such grafts in the nursery are normally re-

It was while removing them that the cases under report, i.e. flowers appearing from rootstock stems were discovered. On the whole, however, 269 Bombai, 628 Langra and 205 Fazli grafts, only 12, 1 and 7, respectively, produced panicles from their rootstock stems. In all these cases the rootstock shoots had also produced flowers.

Maintained jointly by the Imperial Council of Agricultural Research, India, and Government of Bihar in the Department of Agriculture

In four of the Bombai and two Fazli grafts the flowers appear on the root-stock stem also set fruit (Plate XVIII, figs. 1, 2).

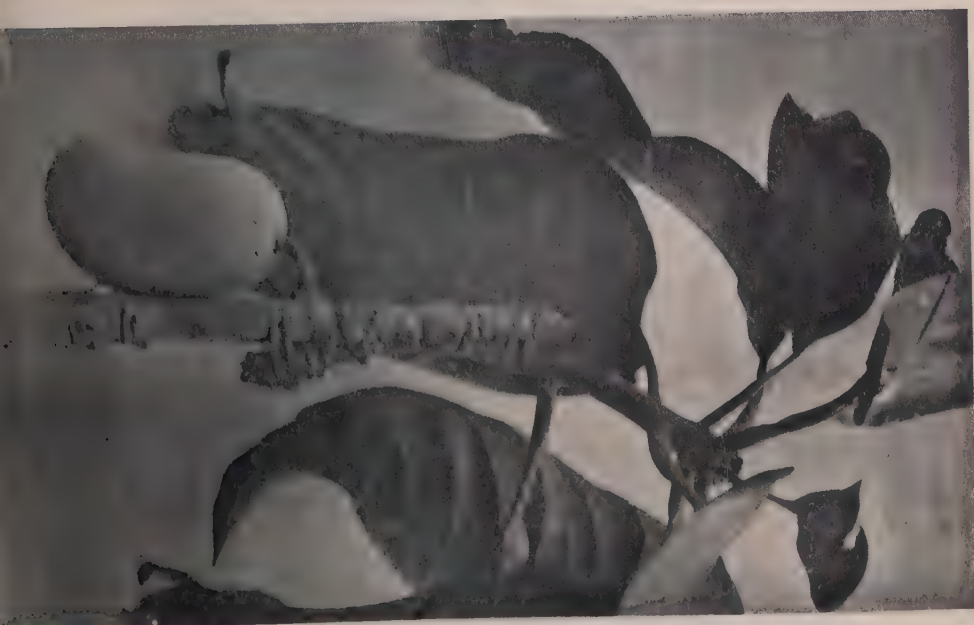
Mango grafts have been prepared in large numbers for over thirty years at Sabour but this is the first occasion when the phenomenon in question has been noted. It is possible that nursery men and research workers elsewhere have noticed this phenomenon some time or other but it is by no means of common occurrence.

An elucidation of the factors that induced flowering from rootstock in such grafts, would appear to be of great interest and importance in connection with studies on factors governing fruit-bud formation. It was thought that lopping the rootstock stem above the graft union and the smudging caused by the grafting bandage had an effect. These two factors are, however, always in association with grafting, but the phenomenon in question appears to be only occasional. It is also known that the tree can be made to flower by means of smudging at any time of the year provided that the tree is in condition for forcing [Gonzalez, 1923]. Smudging can not, however, induce flowering if the shoot bud will not form reproductive organs [Alcala and Pedro, 1935]. In the present cases, however, the effect of smudging does not arise as the grafts were not in any way subjected to such stimulation. The writer suggests that it is not unlikely that the stock had exerted some influence on the rootstock in some way or other. The scion parent trees were in a very favourable condition for fruit bud formation during the period of grafting. After inarching, when the union of the scion and the scion shoot was effected, even when the latter was yet on the stock tree, metabolic translocation between the stock and the scion shoot was possible. Where the scion was in a very favourable condition for fruit bud formation, it is likely that the stock was also brought up to a similar condition of such condition.

The observations are recorded here in the belief that they might be of interest to botanists and horticulturists.

REFERENCES

- Gonzalez, L. G. (1923). *Philipp. Agriculturist* **12**, 23.
Alcala, E. P. and Pedro, S. S. (1935). *Philipp. Agriculturist* **24**, 27-8



LANT QUARANTINE NOTIFICATIONS

tion No. F. 193/40-A., dated 15th December 1941, issued by the Govern-
ment of India in the Department of Education, Health and Lands

exercise of the powers conferred by sub-section (1) of Section 3 of the
Insective Insects and Pests Act, 1914 (II of 1914), the Central Govern-
ment is pleased to direct that the following further amendments shall be made
in the Order published with the notification of the Government of India in
the Department of Education, Health and Lands, No. F. 193/40-A., dated
15th February 1941, namely :—

In clause (a) of paragraph 2 of the said Order—

i) after the word "permit" the words "in accordance with the
form set forth in the Schedule to this Order" shall be inserted,
and

ii) after the word "behalf" the following proviso shall be inserted,
namely :—

'Provided that a permit shall not be refused in the case of any
insect which, in healthy condition, is not likely to be destruc-
tive to crops'.

To the said Order, the following Schedule shall be added, namely :—

' SCHEDULE

Form of special permit authorising importation of insects

Name, designation and full address of the importer.....

.....

Name of the insect species to be imported.....

Stage or stages of the insect to be imported.....

Country from which importation is sought.....

Whether importation is intended by sea, land or air.....

Whether in its original home it is a weed pest, a parasite or a preda-
tor.....

.....

(i) Name (names) of the weed (weeds) on which it is a pest in the
country of origin.....

(ii) Name (names) of the pest (pests) on which it is a parasite or predator
in the country of origin.....

Name, designation and address of the exporter.....

Quantity indented for.....

Purpose of importation.....

The above information is true to the best of my belief.

.....

(Signature of the importer).

I hereby authorise the importation. This permit will be valid up to.....

.....

(Signature and designation of the
certifying authority)

B.—It is expected that the permit will be obtained in advance of
the order, so that the imported material may not remain indefinite-
ly in the warehouse without want of suitable permit]

ERRATA

THE INDIAN JOURNAL OF AGRICULTURAL SCIENCE, VOL. XII, PART I, FEBRUAR

Page 15, line 23, from below, for ' Author ' read ' Another '

Page 22, line 19, for ' $30.53 \ 0.41$ ' read ' 30.53 ± 0.41 '

Page 22, line 21, for ' $0^{\circ} - 2^{\circ}$ ' read ' $30^{\circ} \pm 2^{\circ}$ '

Page 22, line 23, for ' 941 ' read ' 1941 '

Page 26, Fig. 2, figures along abscissa, for ' $5^{\circ}\text{C.}, 10^{\circ}\text{C.}, 5^{\circ}\text{C.}, 0^{\circ}\text{C.}, 5^{\circ}\text{C.}, 0^{\circ}\text{C.}, 5^{\circ}\text{C.}$ ' read ' $5^{\circ}\text{C.}, 10^{\circ}\text{C.}, 15^{\circ}\text{C.}, 20^{\circ}\text{C.}, 25^{\circ}\text{C.}, 30^{\circ}\text{C.}, 35^{\circ}\text{C.}, 40^{\circ}\text{C.}$ respectively '

Page 27, last line, for ' soil temperature ' read ' soil-temperature '

Page 28, line 1, for ' or ' read ' for '

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